Optical Transition and Electrical Conduction Mechanisms in Plasma Polymerized 2, 6-Diethylaniline Thin Films

Ph. D. Thesis

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The thesis titled "OPTICAL TRANSITION AND ELECTRICAL CONDUCTION MECHANISMS IN PLASMA POLYMERIZED 2, 6-DIETHYLANILINE THIN FILMS" submitted by RUMMANA MATIN Roll No-P04081401F, Registration No. 1005370, Session: April/2008 has been accepted as satisfactory in partial fulfillment of the requirement for the degree of Doctor of Philosophy (Ph.D.) on 24 July 2013.

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Declaration

It is hereby declared that this thesis or any part of it has not been submitted elsewhere for the award of any degree or diploma.

Signature of the candidate

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DEDICATED

To

MY PARENTS
AND
MY HUSBAND
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Glossary

a Acceleration of an electron
$a$ Unit lattice cell dimension
$A_R$ Richardson constant
ABS Absorbance
AC Alternating Current
AFM Atomic force microscopy
Al Aluminum
c Velocity of light
$C$ Capacitance
$\Delta C_p$ Change in heat capacity
CA Contact angle
Cr-Al Chromel-Alumel
CBD Chemical Bath Deposition
d Sample thickness
distance between neighboring potential wells
DC Direct current
DEA 2,6 Diethylaniline
DSC Differential scanning calorimetry
DTA Differential thermal analysis
$E$ Electric field
$\Delta E$ Activation energy
$E_g(d)$ Direct optical transition energy gap
$E_g(i)$ Indirect optical transition energy gap
$E_u$ Urbach energy
EDX Energy dispersive X-ray
ESR Electron spin resonance
$f(E)$ Electron energy distribution
$f_{\text{max}}$ Frequency of maximum loss
$F$ Force constant of bond
$F_s$ Static electric field
FL Fermi level
FTIR Fourier transform infrared
$G$ Conductance
$H$ Heat
$h$ Planck’s constant
$h_1$ PPDEA heat treated at 473 K
$h_2$ PPDEA heat treated at 573 K
$\hbar$ Reduced Planck’s constant
$I$ Current
$I_r$ Intensity of radiation
IR Infrared
$k_B$ Boltzmann constant
$K$ Extinction co-efficient
Kelvin
$m$ Mass
$m_e$ Mass of electron
$m_m$ Mass of particles (neutral atoms and molecules).
N Nitrogen
$N_2$ Nitrogen gas
$N$ Number of charge carriers
$N_g$ Gas density
$N_e$ Effective density of states in the conduction
$N_i$ band Density of trapping levels
$n$ Frequency exponent
$n_e$  
Electron density

$P_g$  
Plasma pressure

PECVD  
Plasma enhanced chemical vapor deposition

PPDEA  
Plasma Polymerized 2, 6 Diethylaniline

PPDP  
Plasma-polymerized Diphenyl

PPm-X  
Plasma-Polymerized m-Xylene

PPAn  
Plasma-Polymerized Polyaniline

PVD  
Physical vapor deposition

RF  
Radio frequency

SCLC  
Space charge limited conduction

SEM  
Scanning electron microscopy

$t$  
Time

$T$  
Temperature

$T_d$  
Thermal degradation temperature

$T_e$  
Electron temperature

$T_c$  
Crystalline temperature

$T_g$  
Glass transition temperature

$T_i$  
Ion temperature

$T_{in}$  
Initial temperature

$T_{fi}$  
Final temperature

$T_m$  
Melting temperature

$T_o$  
Onset temperature of thermal degradation

$T_w$  
Water/moisture evolution temperature

TGA  
Thermogravimetric analysis

$\tan \delta$  
Dielectric loss

UV-vis  
Ultraviolet-visible

$V$  
Voltage

$V_i$  
Ionization potential of the atom

Wt %  
Weight percent

XPS  
X-ray photoelectron spectroscopy

XRD  
X-ray diffraction

$\alpha$  
Absorption coefficient

$\beta_{ep}$  
Experimental $\beta$ co-efficient

$\beta_s$  
Schottky co-efficient

$\beta_{PF}$  
Poole-Frenkel co-efficient

$\varepsilon'\,$  
Dielectric constant

$\varepsilon''\,$  
Dielectric loss factor

$\varepsilon_0\,$  
Permittivity of free space or static dielectric constant

$\varepsilon^*\,$  
Complex dielectric permittivity

$\phi$  
Coulombic barrier height

$\phi_0$  
Coulombic barrier height

$\Phi_{SBH}$  
Schottky barrier height

$\phi_i$  
Ionization potential of the Poole-Frenkel centers

$\phi_{im}$  
Image potential

$\lambda$  
Wavelength

$\lambda_e$  
Mean free path of electrons

$\mu$  
Mobility of charge carrier

$\nu$  
Photon

$\theta$  
Trapping Factor

$\sigma_s$  
Steepness parameter

$\sigma_{dc}$  
DC electrical conductivity

$\sigma_{ac}$  
AC electrical conductivity

$\tau$  
Relaxation time

$\tau_p$  
Residence time for a gas molecule in plasma

$\omega$  
Angular frequency

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Abstract

Deposition of the plasma polymerized 2, 6 diethylaniline [(C₂H₅)₂C₆H₃ NH₂] (PPDEA) thin film is carried out by using a capacitively coupled glow discharge reactor after optimizing the plasma deposition parameters. Thermal, surface morphological, structural and optical properties of as-deposited PPDEA thin films are compared with those of the heat treated, aged and iodine doped as-deposited ones by using different characterization techniques. The electrical properties of as-deposited and iodine doped as-deposited PPDEA thin films are also investigated.

The thermal analyses reveal that PPDEA is thermally stable up to about 580 K whereas, the thermal stability is increased up to about 650 K after heat treatment at 573 K. Iodine doping has not caused any significant effect on thermal stability. The glass transition temperature (T_g), is found about 275 and 290 K and the heat capacity (∆C_p) at T_g is calculated out to be about 121.8 and 357 J/kg-K for as-deposited and heat treated PPDEA thin films respectively. Scanning electron microscopy shows uniform and pinhole free surface for both of the as-deposited and heat treated (573 K) PPDEA thin films and the surface become much smoother after iodine doping. The Electron dispersive X-ray analysis has detected C, N and O in as-deposited and heat treated PPDEA thin films and iodine in iodine doped ones. Fourier transform infrared spectroscopic analyses have revealed the retention of aromatic ring structure and ethyl group of the starting monomer in PPDEA structure along with some rearrangement/cross-linking due to plasma polymerization technique. Heat treatment caused some structural rearrangement and iodine doping has showed a little increase/decrease in band intensity and shift in few absorption bands which suggests modification of bond length. The allowed direct and indirect optical transition energy gaps (E_g) of as-deposited PPDEA thin films of different thicknesses are found about 3.63 and 2.23 to 2.38 eV respectively. The E_g values decrease after heat treatment and iodine doping and also with the doping period but not changed appreciably after aging. The other optical parameters (Urbach energy, steepness parameter and extinction coefficient) of as-deposited PPDEA thin films are also changed after heat treatment and iodine doping but are not changed appreciably after aging. Iodine doping increased the direct current electrical conductivity of as-deposited PPDEA thin films of different thicknesses at different temperatures and the electrical conduction mechanism of Schottky type dominating in as-deposited PPDEA thin films is changed to Poole-Frenkel after iodine doping which might have resulted due to the charge transfer complex formation through donor type PPDEA and acceptor type iodine. The increase in activation energy, (∆E) from low to high temperature region of both types of (as-deposited and iodine doped as-deposited) PPDEA thin films may be attributed due to a transition from a hopping regime to a
regime dominated by distinct energy levels. The higher value of \( \Delta E \) of as-deposited PPDEA thin films compared to that of the iodine doped ones most possibly be due to the extra carrier generation which ensues the lower energy to activate the carriers to conduct through the PPDEA thin films. The alternating current (AC) electrical conductivity (\( \sigma_{ac} \)) of both types of PPDEA thin films increases as frequency increases for all the temperatures scanned. The values of frequency exponent, \( n \) of both types of PPDEA thin films corresponds Debye-type and other than Debye type relaxation process in the lower and higher frequency region respectively. The temperature dependence of \( \sigma_{ac} \) of both types of PPDEA thin films suggest hopping of carriers between the localized states. The behavior of dielectric constant (\( \varepsilon' \)), of both types of PPDEA thin films indicates space charge or interfacial polarization and dipolar polarization at lower and higher frequency regions respectively. At higher temperature region (373 to 398 K) the increase of maximum value of loss tangent, \( \tan\delta \) with increasing temperature implies increase of carriers by thermal activation. The increase in \( \sigma_{ac} \), \( \varepsilon' \) and \( \tan\delta \) after iodine doping can be explained on the basis of the formation of charge transfer complex.
1.1 Introduction

Plasma polymerization is one of the modern techniques to deposit uniform, pinhole-free and flawless thin polymer film on any surface that is in contact with the plasma of the organic monomer. It is a unique and rather unconventional thin film technology which yields polymers having properties completely different from those of conventional polymers. This is a distinctive technique for direct thin film deposition of different kinds of polymeric materials of organic monomers. [1-3].

A variety of techniques for producing polymer thin films have been utilized. Thin polymer films can be prepared in two ways: one includes wet processes like Langmuir-Blodgett, spreading, dipping, or solvent casting methods. The other is dry processing, such as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Among various polymer synthesizing methods, glow discharge plasma polymerization is frequently used to make polymer thin films, in which free electrons gain energy from an imposed electrical field, and subsequently the dissociation of covalent bonds in gas phase molecules occurs through collisions between energetic species, such as ions, electrons, photons, and excited neutrals created in the glow discharge. The transfer of energy to gas molecules leads to the formation of a host of chemically reactive species, some of which become precursors to the plasma polymerization reaction. Although the recognition of thin film formation by glow discharge polymerization can be traced back to 1874, and of chemical reactions in electrical discharges to 1868, systematic investigation of plasma polymerization began only in the 1960s.

Plasma polymers are deposited on surfaces contacting a glow discharge of organic or organometallic feed gases in the form of a thin film and/or as a powder. Plasma polymerization is a specific type of plasma chemistry, which involves reactions between plasma species, between plasma and surface species and between surface species that is why in most cases branched and cross-linked polymer thin films are formed. In the case of free radical mechanism, two types of reaction can be postulated: i) plasma induced polymerization and ii) plasma state polymerization. Plasma induced polymerization is the conventional free-radical induced polymerization of molecules containing unsaturated carbon-carbon bonds, while plasma state polymerization depends on the presence, in a plasma, of electrons and other species energetic enough to break any bond. A cursory survey of the literature concerning plasma polymerization reveals that due to the complexity of plasma the bulk of the research has been concentrated on establishing the dependence of
the macroscopic and spectroscopic properties of the product on the major process variables e.g. power, monomer type, gas flow rate, pressure, etc.

Yasuda [4] proposed the Competitive ablation and polymerization (CAP) mechanism for glow discharge polymerization. By combining a certain number of kinetic modeling studies Bell et al. [1] reported a model for the plasma polymerization of hydrocarbons. A more general description was given by Yasuda who identified two regimes of plasma polymerization in which the mechanisms differ dramatically i.e. the monomer - deficient and the energy deficient plasma.

Plasma polymerization is a dry method and in the field of direct thin film deposition this method is becoming one of the fastest growing methods in contradistinction to the conventional polymerization methods. The plasma polymer films have cross-linked structure and have good chemical and physical stability. Moreover, the thin films obtained by plasma polymerization are generally homogeneous and adherent. These thin films have a growing interest for study as active components widely used in electronics and optoelectronics. The charge transport mechanisms in these plasma polymerized organic thin films of a few nanometers are interesting enough because of its uniformity which has been studied in recent years owing to their fabrication as insulating, dielectric and functional layers for electronic functional elements such as thin film transistors, diodes, switching elements, photovoltaic devices, dielectric capacitors, etc. Due to the application potentiality some of the polymers, e.g. polyaniline (PAn), polypyrrole (PPy), polythiophene (PTH), polyacetylene and their derivatives, stimulated vast research activity.

Yasuda [4] surveyed 28 monomers and found that monomers containing aromatic groups, nitrogen (N) (e.g., -NH, -NH₂, -CN), silicon and olefinic double bonds are more polymerizable while those containing oxygen (O) (e.g. –C=O, -O-, -OH), chlorine, aliphatic hydrocarbon and cyclic hydrocarbon tend to decompose.

Several excellent papers have been published on the structural, morphological, optical and electrical properties of thin films prepared by different techniques (plasma polymerization, solution cast, thermal evaporation, vacuum-deposition, radio-frequency magnetron sputtering, spin-coat, etc.) [5-51]. Among them plasma polymerized organic conjugated polymer thin films have received great attention in recent years for their increasing number of applications in a wide verity of fields. Most investigators studied the optical properties such as direct ($E_{g(d)}$) or indirect ($E_{g(i)}$) transitions and other optical parameters of plasma polymers. Simultaneously the electrode and bulk limited conduction processes which are operative in these films have also been frequently reported. The optical and electrical
conduction mechanisms are also studied based on their thermal, elemental and structural properties [5-25, 27, 28, 35-40, 48-51]. Plasma polymer films have been employed to increase the adhesion and compatibility in immiscible systems. Their good adhesion to metals, ceramics, and other polymers has potential applications to adhesion promoters, surface protective coatings, etc. For this reason many investigations were made on their morphological, structural and chemical properties [31-38].

1.2 Literature Review

1.2.1 Reviews on Polymers and Plasma Polymers

Plasma polymerized thin organic film gains increasing scientific interest for their optical and electrical properties suitable for different devices. Plasma polymerized films have molecular structures different from the conventional polymers. The most significant is that the plasma polymer films have cross linked structure so that these films are chemically and physically stable. The thermal, optical and electrical properties of different organic polymer thin films have attracted a great deal of attention from researchers [1,2,3].

Bhuiyan and Bhoraskar [6] investigated the electrical and optical properties to see the extent of conjugation in the pyrolysed system of the thin films of plasma-polymerized acrylonitrile (PPAN) deposited by glow discharge polymerization. The onset and building up of conjugation due to the structural modifications was investigated by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and infrared (IR) spectroscopy. A major structural transition was observed at around 550 K which was responsible for the drastic reduction in the electrical resistivity and optical band gap ($E_g$). ESR studies revealed that pyrolysis causes conjugation and generation of free radicals in PPAN, thereby enhancing the electrical conductivity. The mechanism of conduction was observed to be dominated by the variable-range hopping.

Zaman and Bhuiyan [7] deposited plasma polymerized tetraethylorthosilicate (PPTEOS) thin films by a capacitively coupled parallel plate glow discharge reactor. From EA and IR spectroscopic analysis they showed that the PPTEOS film deposited by the plasma polymerization technique does not exactly resemble to that of monomer tetraethylorthosilicate (TEOS) structure. From UV-vis spectroscopy it was found that the $E_{g(d)}$ is 3.00 eV and the $E_{g(i)}$ is 1.28 eV.
Chowdhury and Bhuiyan [8] investigated the plasma polymerized diphenyl (PPDP) thin films which were deposited using a capacitively coupled glow discharge reactor and showed that the $E_{g(d)}$ and $E_{g(i)}$ values were changed due to heat treatment and aging. Shahjalal et al. [9] deposited plasma polymerized m-Xylene (PPm-X) thin films using a capacitively coupled glow discharge reactor. From the UV-vis spectroscopic analyses the optical band gap energy ($E_g$) of about 3.61 eV was obtained for as-deposited PPm-X thin films. The $E_g$ was increased for both heat treated and aged thin films.

Sarker and Bhuiyan [10] investigated on plasma-polymerized 1-benzyl-2-methylimidazole (PPBMI) thin films. The Fourier transform infrared (FTIR) spectroscopic analyses showed that the chemical composition of PPBMI thin films was different from that of the monomer. From the UV-vis absorption spectra the $E_{g(d)}$ and $E_{g(i)}$ were determined for as-deposited PPBMI thin films of different thicknesses. Both $E_{g(d)}$ and $E_{g(i)}$ values were increased with increasing film thickness and were decreased upon heat treatment. Kamal and Bhuiyan [11] deposited plasma-polymerized pyrrole (PPPy), PPTMA and PPPy-PPTMA bilayer thin films on to glass substrates at room temperature by a capacitively coupled parallel-plate reactor. The structural analyses by FTIR spectroscopy have indicated that the chemical structure of monomer has undergone the reorganization and the ring structure is retained during the plasma polymerization. From the UV–vis absorption spectra, $E_{g(d)}$ and $E_{g(i)}$ were determined and it is seen that the $E_g$ values of the PPPy-PPTMA bilayer films have been increased compared with the PPPy and PPTMA films. Afroze and Bhuiyan [12] investigated on plasma polymerized 1, 1, 3, 3-tetramethoxy-propane (PPTMP) thin films of different thicknesses. The infrared spectroscopic investigation has indicated the formation of conjugation along with C=O bonds in as-deposited PPTMP thin films. The $E_{g(d)}$ and $E_{g(i)}$ were found to be about 2.92 to 3.16 eV and 0.80 to 1.53 eV respectively for as-deposited PPTMP samples of different thicknesses. The $E_{g(i)}$ of two samples of different thicknesses heat treated at 673 K were found to be 0.55 and 0.65 eV. Tamirisa et al. [13] synthesized polyaniline (PAn) thin films on several substrates positioned at various distance from the center of the coil of an inductively coupled pulsed-plasma reactor. FTIR spectroscopy results revealed that the chemical composition and structure of the films were very dependent on the substrate’s position with respect to the radio frequency (RF) coil. Scanning electron microscopy (SEM) studies indicated that as the films became thicker they developed nodules atop a somewhat smoother underlayer.
Several investigations were carried out on PPy thin films. John et al. [14] found that iodine doping increased the conductivity of the plasma polymerized (PPPy) thin film and decreased the optical $E_g$. A comparative study of the IR spectra of the monomer and the PPy gave information that the ring structure was retained during plasma polymerization. Silverstein et al. [15] investigated structural and optical properties of plasma polymerized thiophene (PPTh) and found that the PPTh films differed from the monomer structure. The band gap for the PPTh films is similar to that for conventional PTh.

Cho and Boo [16] deposited Nitrogen-doped thiophene plasma polymer (N-ThioPP) thin films by radio frequency (13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) method. Thiophene was used as organic precursor (carbon source) with hydrogen (H) gas as the precursor bubbler gas. Additionally, nitrogen gas ($N_2$) was used as N dopant. Furthermore, additional argon (Ar) was used as a carrier gas. The as-grown polymerized thin films were analyzed using ellipsometry, FTIR spectroscopy, Raman spectroscopy, and water contact angle (CA) measurement. The ellipsometry results showed the refractive index change of the N-ThioPP film. The FTIR spectra showed that the N-ThioPP films were completely fragmented and polymerized from thiophene. NHx species was increased by increasing the $N_2$ flow rate. Also, decreasing the CA shows the increasing surface energy of the N-ThioPP thin film with increasing $N_2$ flow rate. Additionally, decreasing the contact angle indicates the indirect cause of the increasing N amounts in the N-ThioPP thin film. N atoms bonded with thiophene molecules during the PECVD process. UV-Vis spectra of all samples show 80% of transmittance in the infrared region. However, transmittance in the visible region was dramatically changed by increasing the N amounts. Thus, the $E_g$ of N-ThioPP was increased by increasing the N amounts.

Choi et al. [17] fabricated plasma-polymerized Polyethylene glycol (PP-PEG) thin films on various substrates by using PECVD method and PEG200 as a precursor. The structure of the PP-PEG thin film was found to be very similar to the chemical structure of a PEG. In this study, they modified the PP-PEG thin film with a simple $H_2/He$ plasma treatment to change the non-fouling surface property to a fouling one for proteins and cells. Various surface analysis techniques such as water CA, atomic force microscopy, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry were used to confirm the drastic changes in the surface chemical properties resulting from the plasma treatment. These results show that a PP-PEG film, together with its plasma treatment through a shadow mask, is a very simple and useful patterning technique for various biological applications.
Jiang et al. [18] investigated the surface O in three types of plasma polymerized thin films by XPS, FTIR and electron spin resonance. The results demonstrated that the formation and distribution of O on and within the plasma polymerized films are strongly dependent upon the chemical composition and structure of the films.

Anderson and Jacob [19] prepared linalyl acetate thin films by RF plasma polymerization technique between RF power levels of 10 to 75 W. The UV-vis spectroscopy between 200 to 1000 nm thin films revealed the $E_g$ of approximately 3 eV for all power levels.

Bazaka and Jacob [20] prepared RF plasma polymerized thin films of Terpinen-4-ol of different thicknesses (100-1000 nm) by varying the deposition time. The $E_g$ estimated to be 2.67 eV confirmed the possibility of using the polymer film in semiconductor applications.

Easton and Jacob [21] investigated the ageing effect and thermal degradation of plasma polymerized thin films derived from the essential oil of Lavandula angustifolia (LA). Spectroscopic ellipsometry and FTIR spectroscopy revealed that the bulk of the degradation under ambient conditions was found to occur within the first 100 h after fabrication. An increase in thermal stability was found for films fabricated at increased RF power levels. The refractive index values signify a phase change in the material between 473 and 573 K for all samples. The FTIR spectra of the polyLA film heated to this temperature range indicated loss of H from the chemical structure via elimination of water and the subsequent formation of C–O or C=C bonds.

Electrical conduction in polymers has been studied extensively during the last couple of decades to understand the nature of charge transport in these materials. Their conduction mechanism varies depending on their variations in synthesis, deposition condition and doping procedures. Various mechanisms, such as Schottky emission, Poole-Frenkel (PF) emission, and Space-charge limited conduction (SCLC) have been suggested for the charge transport [22, 6]. The first of various electrically conductive polymers was polyacetylene. Other specialty polymers in this class that have been extensively studied include PAn, PTh, poly (p-phenylene) and PPy [48].

Sarker and Bhuiyan [23] investigated on the electrical properties of AC PPBMI thin films to determine the dominant carrier transport mechanism under static electric field. FTIR spectroscopy was employed for structural analysis of the monomer and that of the PPBMI. The FTIR analyses demonstrate that the chemical structure of PPBMI thin films is changed to some extent from that of the monomer. Current density–voltage ($J-V$) characteristics were studied over the temperature range from 300 to 423 K for PPBMI thin films of thicknesses 100, 150, 200 and 250 nm in Al/PPBMI/Al sandwich configuration. The dominant
conduction mechanism in PPBMI thin films is found to be SCLC. The activation energy ($\Delta E$) for the conduction mechanism is found to be 0.43 eV. Carrier mobility, free carrier density and trap density are found to be $1.48 \times 10^{-18}$ to $6.35 \times 10^{-18}$ m$^2$ V$^{-1}$ s$^{-1}$, $1.59 \times 10^{23}$ to $5.85 \times 10^{23}$ m$^{-3}$ and $2.50 \times 10^{24}$ to $5.00 \times 10^{23}$ m$^{-3}$, respectively.

Majumder and Bhuiyan [24] revealed from plasma polymerized vinylene carbonate (PPVC) thin films that the $J-V$ characteristics follow a power law of the form $J \propto V^n$, where $n$ has different values. In the low voltage region $0.85 < n < 1.00$ and those in the high voltage region lie between $1.30 < n < 1.75$, indicating Ohmic conduction in the low voltage region and non Ohmic conduction in the high voltage region. In addition, at higher temperature the $J$ increased significantly revealing a temperature dependence of $J$. Theoretically calculated values and experimental results of Schottky and PF coefficients show that the most probable conduction mechanism in the PPVC thin films is of Schottky type.

Chowdhury and Bhuiyan [25] investigated on plasma polymerized diphenyl (PPDP) films, deposited using a capacitively coupled glow discharge reactor. The IR analysis reveals that the heat-treated PPDP film structure is different from that of the monomer diphenyl. The $J-V$ characteristic revealed that PF conduction mechanism is operative in the heat-treated PPDP thin films.

Nagaraj et al. [26] studied the current-voltage ($I-V$) characteristics of doped polyvinyl films prepared by solution cast technique as a function of film temperature and dopant concentration and found that the dominant charge transport mechanism in this film is Schottky type.

Johan and Sakthi [27] found that iodine doping increased the conductivity of the plasma polymerized PPy film and decreased the optical $E_g$. A comparative study of the IR spectra of the monomer and the PPy gave information that the ring structure was retained during plasma polymerization.

Silverstein et al. [28] investigated structural, electrical, optical properties of PPTh and found that the PPTh films differed from the monomer structure and the $E_g$ for the PPTh films is similar to that for conventional PTh. Undoped films exhibited nonlinear $I-V$ behavior typical of Schottky metal-semiconductor barrier with breakdown at reverse bias. Iodine doping yielded Ohmic $I-V$ behavior.

Tayyan et al. [29] reported on direct current (DC) electrical conduction of iodine doped poly (9-vinylcarbazole) films at various dopant concentrations and film thicknesses. The current-electric field dependence indicated that the electrical conduction is governed by Schottky mechanism.
Gould and Shafai [30] investigated the electrical properties of evaporated lead phthalocyanine thin films with aluminum (Al) electrodes. It is found that the conduction of these films increases as the temperature increases with a thermal $\Delta E$ of $\sim 0.47 \text{ eV}$. Electronic conduction has been investigated in contrast to previously investigated samples where the injecting electrode was a gold ohmic contact, these samples did not exhibit SCLC mechanism, but showed carrier excitation via a field-lowering mechanism with a $\log J \propto V^{1/2}$ $J$-$V$ characteristic. Both polarities showed two regions in the $J$-$V$ characteristics, having different slopes, leading to the conclusion that conduction is via Schottky and Poole-Frenkel emission at lower and higher voltages respectively. In the presence of air there was a decrease in conductivity, which was attributed to the effects of O at the electrodes.

Thin polymer films obtained by means of plasma polymerization are well known to contain a certain quantity of polar groups independent of whether the monomer used was polar or non-polar in the process. The presence of polar groups is one of the significant factors responsible for the relatively high (for polymeric materials) dielectric losses in plasma polymers and is usually suitable for dielectric relaxation studies. It is much more difficult, however, to relate there dielectric relaxations to segmental motions, simply because their structure is not as well defined as the structure of conventional polymers. Another possible reason for the different dielectric behavior of plasma polymers is their very small thickness. Some dielectric parameters especially dielectric strength depends strongly on the thickness of the specimen. When measuring dielectric properties of plasma polymerized films, one operates with thickness of $\sim 1000 \text{ Å}$ or even less, and in this range the bulk properties of materials are already influenced by their surface properties [4].

In recent years, the dielectric and electronic properties of polymeric and organic thin films have received a great deal of interest because of their importance in many advanced applications such as organic light emitting diodes (LED), sensors, rechargeable batteries, electroluminescent devices and as intermetallic dielectrics in integrated circuits (IC) [31]. Chowdhury and Bhuiyan [32] prepared plasma polymerized diphenyl (PPDP) thin films and the dielectric relaxation spectroscopy was employed to investigate the behavior of the as-deposited and heat treated PPDP thin films. It was found that the alternating current (AC) conductivity ($\sigma_{ac}$) is more dependent on temperature in the low frequency region than in the high frequency region and the conduction may be dominated by hopping of carriers between the localized states at low temperatures and thermally excited carriers from energy levels within the band gap in the vicinity of high temperature. The dielectric constant ($\varepsilon'$) is dependent on frequency above 303 and 343 K in the as-deposited and heat treated PPDP,
respectively. The as-deposited PPDP shows superposed $\alpha$ and $\beta$ relaxation processes. For different relaxation processes, the activation energies are estimated to be about 0.45 and 0.67 eV for as-deposited and 1.35 eV for heat-treated PPDP.

Gonon and Sylvestre [33] investigated the dielectric properties of fluorocarbon thin films deposited by RF magnetron sputtering of polytetrafluoroethylene. The $\varepsilon'$ and dielectric loss ($\varepsilon''$) are studied as a function of frequency (0.1 Hz to 1 MHz), IR frequencies and temperature (room temperature to 100 °C). The value of the $\varepsilon'$ is 1.8 at optical frequencies, and around 2.3 in the 0.1 Hz to 1 MHz range. The background loss factor is around 0.8% in these samples. Two different polarization mechanisms are identified ($\beta$ and $\gamma$ relaxations). Temperature dependence of the $\varepsilon'$ is well described by a simple Debye model (linear variation of the $\varepsilon'$ with $1/T$). The $\gamma$ relaxation is tentatively ascribed to C$_2$F bonds. The $\beta$ relaxation has a loss peak located at very low frequencies (<0.1 Hz). It leads to an increase of loss below 10 Hz when temperature is increased above 75 °C. The high-frequency part of the $\beta$ loss peak decreases as $\omega^{-0.35}$. Study of its temperature dependence leads to the $\Delta E$ of 0.66 eV.

Goswami and Varma [34] showed the dielectric properties of vacuum-deposited dysprosium oxide films in the audio-frequency range ($10^2$ to $10^4$ Hz) at various temperatures (78–373 K). The $\varepsilon'$ was independent of film thickness for thicker films ($d > 1000 \text{ Å}$). The capacitance ($C$) was dependent both on temperature and frequency, but became constant for all frequencies at low temperature. $\tan\delta$ showed a frequency minimum and its variation with frequency and temperature is in agreement with the model proposed earlier by Goswami and Goswami. The breakdown field ($\geq 10^6 \text{ Vcm}^{-1}$) followed the Forlani-Minnaja relation.

Yang et al. [35] investigated the properties of low $\varepsilon'$, plasma polymerized decahydronaphthalene (PPDHN) thin films deposited by PECVD technique. Plasma power significantly affected the $\varepsilon'$ values and thermal stability of the deposited films. As plasma power was increased from 30 W to 90 W, the $\varepsilon'$ of the deposited PPDHN thin films increased from 2.65 to 3.12. With the increase in plasma power, integrated peak areas of C=O stretching and O-H stretching vibrations increased, while that of the CHx stretching vibration decreased. All the PPDHN films were thermally stable to 350°C. Upon annealing at 400 °C, the film deposited at 30 W showed ~35% thickness reduction, while the film deposited at 90 W showed only ~15% thickness reduction. All the deposited thin films showed a leakage current density below $10^{-8} \text{ Acm}^{-2}$ at 1 MVcm$^{-1}$.

Cho et al. [36] deposited plasma polymerized pure ethylcyclohexane thin films on Si(100) substrates at room temperature. H and Ar gases were used as precursor bubbler and carrier
gases, respectively. They investigated the electrical and the physical properties of the plasma polymer thin films at various deposition RF powers and annealing temperatures. The IR spectra showed that the plasma polymer thin films had totally different chemical functionalities from those of the ethylcyclohexane precursor and that the chemical functionalities of the thin films changed with the RF power and annealing temperature. From the AC electrical property measurements, the lowest $\varepsilon'$ obtained was 1.71.

Xu et al. [37] deposited polyallylamine films on Si wafers by RF pulsed plasma polymerization, which were employed as insulating layers of metal-insulator-semiconductor (MIS) capacitors. Multiple frequency $C-V$ measurements indicated that an in-situ heat treatment during film deposition increased the insulator $\varepsilon'$. The $\varepsilon'$, calculated from the $C-V$ data, rose from 3.03 for samples with no heat treatment to 3.55 for samples with an in-situ heat treatment. For both sample sets, the $I-V$ data demonstrates a low leakage current value (<20 fA) up to 100 V. Capacitance-time measurements were also used to characterize the mobile ions in the polymer that migrate over time with applied voltage. Results indicate that the polymer layers contain few electrically active defect centers and virtually no pinholes. Hysteresis in the $C-V$ curves with differing sweep directions was more pronounced for in-situ heat-treated samples indicative of mobile charge.

Liang et al. [38] demonstrated the effect of film thickness on the electrical properties of polyimide thin films prepared by spin-coat technique. With decreasing film thickness, the $\varepsilon'$ decreased but the conduction current increased. Using IR spectroscopy, polyimide chains were found to be oriented parallel to the electrodes. The dependence of the $\varepsilon'$ values on film thickness were explained by the orientation of polymer chains.

Zhao et al. [39] characterized the plasma polymerized 1-Cyanoisoquinoline (PPCIQ) thin films. From IR, X-ray diffraction and SEM studies it was found that a high retention of aromatic ring structure of the starting monomer was found in the films. As the films were homogeneous it was used for dielectric measurements. The dielectric measurement of PPCIQ thin film deposited at 15W gives a low $\varepsilon' 2.62$, which might be a potential candidate to be used as inter-metallic dielectrics in microelectronics.

Cho et al. [40] studied the dielectric response and the AC conductivity of heavily iodine-doped poly(2-ethynyl-N-hexylpyridinium bromide) (PHEPB) prepared by direct polymerization and by methanol solvent. The samples were doped with iodine and the dielectric and conductance properties were measured in the frequency range from 50 Hz to 1 MHz. The $\varepsilon'$ showed a stronger dispersion in the low frequency region, and the imaginary part, $\varepsilon''$ exhibited a nearly constant slope. The AC conductivity was well described by using
the universal dielectric response, and the DC and AC activation energies that represent the conduction and the relaxation mechanisms were 0.507 and 0.596 eV, respectively. The room temperature conductivity at 1 kHz was found to be enhanced by more than three orders of the magnitude after iodine doping. The impedance Cole-Cole plot suggested that the dielectric relaxation occurred through a non-trivial relaxation mechanism. Quamara et al. [41] presented the temperature and frequency dependent dielectric behaviour for pristine, iodine-doped and annealed polyetherimide (PEI) thin films in the temperature range of 303 to 523 K at various frequencies (120 Hz, 1 kHz, 10 kHz and 100 kHz). In pristine PEI, the rapid decrease in the \( \varepsilon' \) in the temperature range 303 to 373 K is governed by the Kirkwood model whereas the gradual decrease in \( \varepsilon' \) in the temperature range 373 to 473 K is governed by \( \beta \)-relaxation (dipolar) and \( \alpha \beta \)-relaxation (hybrid) processes and are confirmed by the appearance of \( \tan \delta \) loss peaks at 403 and 443 K, respectively. The temperature independence of \( \varepsilon' \) in the temperature range from 473 to 523 K is mainly governed by the \( \alpha \)-relaxation process associated with large segmental groups. In iodine doped samples, an overall increase in \( \varepsilon' \) is attributed to the formation of charge transfer complexes in the polymer structure. A significant decrease in \( \varepsilon' \) in annealed samples below 393 K is due to the suppression of the dipolar relaxation process. Tanwar et al. [42] prepared pure and doped poly(methyl methacrylate) (PMMA) films by solution cast method. They studied dielectric properties at microwave frequency, 8.92 GHz and at 35°C. Iodine, benzoic acid and FeCl3 have been used as dopants. The losses in doped films are found to be larger than in pure PMMA films. The increased losses account for increased AC conductivity in doped films. The increase in conductivity is accounted due to creation of additional hopping sites for the charge carriers in doped samples. For the iodine doped PMMA films, the \( \varepsilon' \) values increased as the iodine content in the sample increased and this was attributed to the presence of highly polarizable molecular iodine.

1.2.2 Review on Polymerization of Aniline and Its Derivatives

Optical and electrical properties of PAn and their derivatives have attracted considerable research interest due to its potential applications in a wide range of fields. These materials have been synthesized due to there unique characteristics, like inexpensive monomer, easy route of synthesis, ease of processing and good chemical and thermal stability which made them as potential materials for the fabrication of transistors, LEDs [43], sensors [44], photovoltaic devices [45], electrochromic devices [46], etc. Aniline and its derivatives have considerable donor strength and this strength increases when an ethyl group is introduced
either on the N atom or in the benzene ring due to the positive indicative and hyperconjugative effects of ethyl groups. For that anilines have been widely used as donors with different acceptors in many charge-transfer complexation studies [47].

Studying on PPTMA thin films, Akther and Bhuiyan [48] revealed that the PPTMA thin films were formed with certain amount of conjugation which modifies on heat treatment. From the UV–vis absorption spectra, $E_{g(d)}$ and $E_{g(i)}$ were determined to be 2.80 and 1.56 eV, respectively. While $E_{g(d)}$ increased a little and $E_{g(i)}$ decreased on heat treatment of PPTMA. Akther and Bhuiyan [49] deposited PPTMA thin film onto glass substrates at room temperature by a capacitively coupled plasma polymerization system. From UV–vis spectroscopy it is found that $E_{g(i)}$ varies from 1.49 to 1.86 eV with film thickness. $J-V$ characteristics indicate that the conduction mechanism in PPTMA thin films is SCLC. The $\Delta E$ in the SCLC region are $0.21 \pm 0.05$ and $0.93 \pm 0.08$ eV at lower and higher temperature regions respectively. Electrical and optical measurements suggest that the top of valance band and the bottom of the conduction band may have gap states and the middle of the energy gap may be equal to the high-temperature $\Delta E$.

Mathai et al. [50] investigated the electrical properties of AC plasma polymerized aniline thin films with a view of determining the dominant conduction mechanism. The $I-V$ characteristics in symmetric and asymmetric electrode configuration for polyaniline thin films in the thickness range from 1300 to 2000 Å are investigated. From the studies on asymmetric electrode configuration, it is found that the dominant conduction mechanism in these films is of Schottky type.

Sajeev et al. [51] prepared the RF and AC PPAn thin films and found that $E_g$ of these films differ considerably and the $E_g$ was further reduced by in situ doping of iodine. It has been shown that electrical conductivity of this film in the case of RF plasma polymerized thin films has a higher value compared to that of AC. Iodine doping enhanced conductivity of the polymer thin films considerably.

Arslan et al. [52] investigated the optical properties of poly(N-benzylaniline) thin film by UV–vis spectroscopy. The $E_g$ of the thin film was decreased with increasing annealing temperatures while the Urbach energy was increased.

Olayo et al. [53] studied about the electric conductivity in PAn synthesized by plasma obtained from halogenated anilines in which chlorine or iodine atoms are bonded in meta position to the aniline rings. The results show that the halogenated anilines produce polymers with an electric conductivity up to eight orders of magnitude higher than those of the undoped PAn, reaching $10^{-4}$ S/cm.
El-Nahass et al. [54] investigated on physical characteristics of 4-tricyanovinyl-N, N-diethylaniline. The differential scanning calorimetry (DSC) showed the stability of this compound up to 423 K. The temperature dependence of the electrical conductivity was found typical for semiconducting compounds. The $J$-$V$ characteristics revealed that, the conduction current obeys Ohm’s law while the charge transport phenomenon appears to be SCLC in the higher voltage region.

Drachev et al. [55, 56] obtained plasma polymerized thin films from 3-methoxythiophene at the cathode in a DC discharge. It was found from FTIR spectroscopy that thiophene rings are the main structural units of the polymer; aliphatic fragments and O-containing groups are also present. The polymer based on 3-methoxythiophene is found to exhibit p-type intrinsic conduction with $\Delta E$ of 0.045 eV. The conductivity of the polymer at 20 °C is found about $10^{-8} \Omega^{-1} \text{cm}^{-1}$ and doping with iodine resulted in a rise in conductivity to $10^{-3} \Omega^{-1} \text{cm}^{-1}$. They also investigated on polymer films as organic semiconductors with an intrinsic conductivity of $~10^{-11} \Omega^{-1} \text{cm}^{-1}$ which were prepared from aniline at the cathode in a DC discharge. The conductivity of the films was increased to $~10^{-2} \Omega^{-1} \text{cm}^{-1}$ by doping with iodine.

Lin and Yuzhong [57] reported the electrical conductivity of iodine doped polyaniline furfural (PAF). The electrical conductivity of iodine-doped PAF is found about $10^{-3} \text{S cm}^{-1}$ which is more than 10 orders of magnitude higher than what is observed at the pristine state. The UV-vis absorption peak of the undoped PAF appeared at about 313 nm. After doping, the optical absorption peak shifted to longer wavelength at around 356.8 nm. This measurement showed that a new conjugated structure forms after doping. FTIR spectra of iodine doped PAF shows a new band at 1549 cm$^{-1}$. The formation of new band is attributed due to the radical cation generated upon charge-transfer. It is inferred that the charge-transfer complex (PAF-Iodine) is formed during doping. The radical cation polarons and dopant anions are formed and contributed to the charge carriers. The charge transport may have involved an intra and inter chain hopping processes.

Stejskal et al. [58] exposed PAn to iodine in an ethanol-water suspension. PAn base reacted with iodine and its conductivity increased by five orders of magnitude. The FTIR results showed that the increase in conductivity is due to protonation of PAn with the hydriodic acid that was produced in the oxidation of the emeraldine base to the pernigraniline form.

Adhikari and Banerji [59] synthesized pristine and iodine doped PAn by the thermal evaporation technique. Iodine doping was carried out by evaporation. From TGA analyses it is interpreted that emeraldine base polyaniline (EB-Pan) powder is stable in air up to 300
°C. The FTIR spectrum of thermally evaporated EB-PAn film is found somewhat different from the conventional PAn spectrum. The peak around 430 nm in UV-vis spectrum have indicated formation of polaron which exhibits a bathochromic shift from 430 to 432 nm on increasing the dopant concentration from 2% to 6%, indicating a decrease in the bandgap of PAn upon iodine doping. The SEM analysis have shown the surface morphology of pristine PAn with small discrete particles having irregular shape while the iodine doped films have shown uniform distribution of fine particles. The undoped film has shown non-ohmic behavior whereas the iodine doped films exhibited ohmic conductivity with Al. The conductivity of the doped films are seen to increase with the iodine concentration and many fold increase in conductivity is observed in comparison to the pristine films. The increase in conductivity is attributed due to the generation of polaron band in the \( E_g \) upon iodine doping.

Akther and Bhuiyan [60] investigated the dielectric properties of PPTMA thin films. In PPTMA thin films the conduction may be dominated by hopping of carriers between the localized states at low temperatures and thermally excited at the high temperatures. The \( \Delta E \) values were estimated to be about 0.05 eV in the low temperature and 0.23 eV in the high temperature. The \( \varepsilon' \) decreased with the increase of frequency and that decreased with the increase of temperature but \( \varepsilon'' \) increased with increasing frequency with a minimum in the low frequency region. The temperature-dependence of the Cole-Cole diagram showed the existence of distribution of dielectric relaxation times in the PPTMA thin films.

Mathai et al. [61] investigated the \( C, \varepsilon'', \varepsilon' \) and \( \sigma_{ac} \) of PAn thin films prepared by AC plasma polymerization technique in the frequency range from 100 Hz to 1 MHz and in the temperature range from 300 to 373 K. \( C \) and \( \varepsilon'' \) decreased with frequency and increased with temperature. The \( \sigma_{ac} \) was found to vary as \( \omega^n \) with the index \( n \leq 1 \). Annealing of PAn thin films in high vacuum at 373K for 1 h was found to reduce the \( \varepsilon'' \).

Nahass et al. [62] reported the dependence of electrical conductivity (DC, AC) and dielectric properties on temperature and on frequency of thermally deposited thin films of N-(p-dimethylaminobenzylidene)-p-nitroaniline (DBN). The DC conductivity indicated a thermally activated carrier hopping rate which increased with increasing temperature. The obtained experimental results of AC conductivity showed that the correlated barrier hopping model is the appropriate mechanism for the electron transport in the DBN film. Both the \( \varepsilon' \) and \( \varepsilon'' \) showed a decrease with increasing frequency.
1.3 Objectives of the Research Work

The optical and electrical properties of PAn have attracted considerable research interest due to its potential applications in a wide range of fields. In our laboratory, investigations have been done on several plasma polymerized organic thin films including N, N, 3, 5 tetramethyl aniline thin film. It has been found that aniline and its derivatives have considerable donor strength. Commonly, the donor properties of the anilines increase when an ethyl group is introduced either on the N atom or in the benzene ring, due to the positive inductive and hyperconjugative effects of ethyl groups. For that anilines have been widely used as donors with different acceptors in many charge-transfer complexation studies. It was found that 2, 6 diethylaniline (DEA) has considerably strong donor properties and a strong charge transfer complex can be formed via introduction of iodine acceptor [48].

Reviewing the early research work it is evident that plasma polymerized thin films derived from different organic monomers especially from aniline/ aniline derivative monomers possess versatile optical and electrical (DC and AC) properties due to their diversified structural properties. The variation in their cross-linked structure results from varying plasma deposition parameters and post deposition modifications. It is also seen that post deposition modification of organic polymer thin films of PAn and there derivatives are extensively studied which have interesting results [7, 50, 51, 57].

The objectives of the thesis work are to prepare thin film of DEA by a well established glow discharge polymerization technique and to investigate the optical transitions and electrical conduction mechanisms (DC and AC) of as-deposited and modified (heat treated, aged and iodine doped) plasma polymerized 2, 6 diethylaniline (PPDEA) thin films. The characterization results will be used to ascertain the changes in the modified PPDEA thin films due to the modifications in contrast to the as-deposited/pure ones.

To get the desired sample deposition, the optimized condition for plasma process parameters would be operated properly. To ascertain the thermal, surface morphological, structural, optical and electrical properties of the as-deposited and modified PPDEA thin films of different thicknesses, the following characterization techniques would be employed. Finally, the findings of the thin film would be analyzed with a view to find their suitability in optical and electrical devices.

(i) Thermal analysis:

The TGA, DTA and DTG would be used to characterize the thermal stability and decomposition and DSC would be used to ascertain the \( T_g \) of the as-deposited /pure, heat treated and iodine doped PPDEA in air and N environment.
(ii) **Morphological and elemental analysis:**
SEM and an Energy Dispersive X-ray (EDX) analysis would be done to investigate the surface morphology and compositional analysis respectively of as-deposited and modified PPDEA thin films.

(iii) **Structural analyses:**
The chemical structure of the DEA monomer, as-deposited and modified PPDEA thin films would be investigated by FTIR spectroscopy. A comparative study between the spectra would be done to ascertain the chemical changes occurred in different PPDEA thin films.

(iv) **Optical properties:**
The UV-vis absorption spectroscopic analyses would be done to determine the optical parameters like optical $E_g$ (direct and indirect transition energy gaps), Urbach energy, steepness parameter and extinction coefficient in as-deposited and modified PPDEA thin films.

(v) **Electrical properties:**

a. **DC Electrical properties:**
In $J$-$V$ measurements, the variation of current density with temperature at different applied voltages of samples of different thicknesses would be measured to specify the charge transport mechanism in iodine doped plasma polymerized 2, 6 diethylaniline thin films. In this study, considering PPDEA as capable to create a charge transfer complex in the presence of iodine the affect of charge transfer complex on conductivity of the PPDEA thin films would be investigated.

b. **AC Electrical properties:**
The AC electrical measurements would be done on PPDEA thin films of different thicknesses at different temperatures to understand the AC conduction mechanism and to explore the dielectric relaxation behavior in the PPDEA thin films. The AC electrical measurements will be performed as functions of both frequency and temperature.

1.4 **Thesis Layout**
The research described in this thesis deals with different physical properties such as thermal, surface morphological, compositional, structural, optical and electrical conduction mechanisms (DC and AC) of as-deposited and modified (heat treated, aged and iodine doped) plasma polymerized 2, 6 diethylaniline (PPDEA) thin films prepared by a bell jar type capacitively coupled plasma polymerization setup. The major portion of the thesis
comprises the discussion on the changes of different physical properties of as-deposited PPDEA thin films due to different modifications.

Chapter 1: This chapter focuses on the introduction part presenting an overview to the area of plasma polymerized thin films, their physical and chemical properties and applications in general. This chapter also contains the reviews of earlier research works on different plasma polymerized thin films and discusses the aim of this thesis work.

Chapter 2: This chapter comprises of the fundamental aspects of plasma, polymer and plasma polymerization. This chapter also deals with the different physical characterization techniques along with their theoretical aspects.

Chapter 3: This chapter discusses the experimental details which contains the plasma polymerization setup, generation of glow discharge, deposition of PPDEA thin film, thickness measurement procedure, optimization of PPDEA thin film deposition condition, experimental techniques for modification of PPDEA thin films, characterizing instruments and their measurements.

Chapter 4: This chapter consists of the results and discussion on the different physical properties of as-deposited and modified PPDEA thin films. The investigated physical properties are thermal (thermal stability, glass transition temperature and specific heat capacity) by DTA, TGA, DTG and DSC, morphological by SEM, compositional by EDX, structural by FTIR, Optical (optical absorption, absorption coefficient, optical transition energy gap, Urbach energy, steepness parameter and extinction coefficient), DC electrical properties (J-V Characteristics, conduction mechanism, activation energy and temperature dependent conductivity) and AC electrical properties (type of conduction mechanism, frequency and temperature dependence of AC conductivity, dielectric constants, dielectric relaxation and loss tangent) are discussed in this chapter on the basis of available existing theories.

Chapter 5: This chapter summarizes and concludes all the findings of different investigations narrated in results and discussion along with the suggestions for further studies.
Finally the thesis ends with the references and an appendix.
2.1 Introduction

The Fundamental aspects of plasma, polymer and plasma polymerization are discussed in this chapter. The details of plasma, classification of polymers, reaction kinetics and growth mechanism in glow discharge plasma polymerization, difference between plasma polymer and conventional polymer and advantages of plasma polymerization are illustrated in this chapter. This chapter also addresses different analytical techniques which are employed at various stages to characterize the samples. A brief outline of the theory of these experimental techniques is considered as a prerequisite for the proper understanding of the methods.

2.2 Fundamentals of Plasma, Polymer, Plasma Polymerization and Plasma Polymerized Thin Films

2.2.1 Plasma

The term plasma was first applied to ionized gas by Dr. Irving Langmuir an American physicist and chemist in 1929. Plasma is a partially ionized gas composed of freely moving electrons, ions and neutral species, there being approximately the same density of positive charges as of negative. The term “Fourth state of matter” often used to describe the plasma state was coined by W. Crooke in 1879 to describe the ionized medium created in a gas discharge. The term fourth state of matter follows from the idea that as heat is added to a solid, it under goes a phase transition usually to a liquid. If heat is added to a liquid the kinetic energy of the molecules become large and it becomes gaseous. The addition of still more energy to the gas, results in the ionization of some of the atoms.
Although 99.9% of the apparent universe exists in a plasma state, there is very little in the way of natural plasma here on earth because the low temperature and high density of the earth. In general, when a molecule is subjected to intense heat, the molecule will ionize. The sun, and other stars in our universe, have temperatures ranging from 5000 to 70,000 K or more, and consist entirely of plasma [1]. Plasma properties are strongly dependent on the bulk parameters. Some of the most important plasma parameters are—

I. The degree of ionization, II. The plasma temperature III. The density, IV. The magnetic field in the plasma region.

In analysis plasmas are far harder to model than solids, liquids and gasses because they act in a self-consistent manner. The separation of electrons and ions produce electric fields and the motion of electrons and ions produce both electric and magnetic fields. The electric
Chapter 2  Introduction and Characterization Techniques of Plasma Polymerized Thin Films

fields than tend to accelerate plasmas to very high energies while the magnetic fields tend to guide the electrons. Plasmas resulting from ionization of neutral gases generally contain equal numbers of positive and negative charge carriers. In this situation, the oppositely charged species are strongly coupled and tend to electrically neutralize one another on macroscopic length-scales. Such plasmas are termed quasi-neutral ("quasi" because the small deviations from exact neutrality have important dynamical consequences for certain types of plasma mode). Strongly non-neutral plasmas, which may even contain charges of only one sign, occur primarily in laboratory experiments: their equilibrium depends on the existence of intense magnetic fields, about which the charged fluid rotates [63, 2].

In the laboratory, Plasma can be created by various techniques such as combustion flames, Electrical discharges, controlled nuclear reactions, shocks and other means. The technique of most interest is the glow discharge. Plasmas produced by this technique are called non-equilibrium or cold plasmas in contradistinction to equilibrium plasmas created by arcs or plasma jets. The term non-equilibrium means that there is no thermal equilibrium between electrons and other neutral species and ions. The ambient temperature of plasma in a plasma polymerization reaction however is generally in the vicinity of 380 to 400 K and remains reasonably constant after a steady-state condition is established.

Based on the relative temperatures of the electrons ions and neutrals, plasmas are classified as thermal (hot plasma) or non-thermal (cold plasma). Thermal plasmas have electrons and the heavy particles at the same temperature i.e. they are in thermal equilibrium with each other. Non-thermal plasmas on the other hand have the ions and neutrals at a much lower temperature (ambient temperature) whereas electrons are much ‘hotter’. Plasma is sometime
referred to as being hot if it is nearly fully ionized or cold if only a small fraction (for example 1\%) of the gas molecules is ionized. Even in ‘cold’ plasma the electron temperature is still typically several thousand degrees. Plasmas utilized in plasma technology (technological plasmas) are usually cold in this sense.

### 2.2.2 Fundamental aspects of plasma physics

This paragraph deals with some of the basic concepts of plasma physics that are useful for the understanding of plasma polymerization. First of all, the negative particles in a glow discharge plasma are mostly electrons, however negative ions are also formed. When an electric field is applied, the electrons gain energy according to Newton’s law,

\[
a = \frac{qE}{m_e}
\]

where \( a \) is the acceleration of the electron, \( q \) is its electric charge, \( m_e \) is its mass, and \( E \) is the electric field. Three different types of collisions can occur between an electron and an atom, depending on the energy \( K_c \) that is transferred to an electron in the atom:

1. \( K_c = 0 \). The electrons in the atom remain in the ground state. The collision is elastic, and causes no change in the structure of the atom.
2. \( 0 < K_c < qV_i \), where \( V_i \) is the ionization potential of the atom. An electron in the atom is excited to a higher energy level, but returns to the ground state in a short time, releasing the gained energy again. The collision is inelastic.
3. \( K_c > qV_i \). The atom is ionized by inelastic collision, and becomes positive with charge \(+q\).

Between the energy level of the ground state and that of the ionized state, a number of other energy levels can exist. An electron in an atom that receives energy from a primary electron can jump to a higher energy level, but after a short period of time (of the order of \(10^{-8}\) s) it falls back to lower energy levels or to the ground state. In this process, the electron's excess energy is released e.g. by emission of a photon. When an electron falls back from energy level \( E_m \) to \( E_n \), the frequency \( \nu \) of this photon is given by:

\[
\hbar \nu = E_m - E_n
\]

where \( \hbar \) is Planck’s constant.

The temperature of colliding species plays an important role on the collision processes occurring in a glow discharge. The electron temperature \( T_e \) in a plasma is given by the following equation,

\[
T_e = \left( \frac{e}{k_B} \right) \left( \frac{E \lambda_e}{2 \sqrt{2}} \right) \left( \frac{m_w}{m_e} \right)^{\frac{1}{2}} \left( \frac{\pi}{6} \right)^{\frac{1}{2}}
\]
in which $k_B$ is the Boltzmann constant, $\lambda_e$ the mean free path of electrons, and $m_m$ the mass of particles (neutral atoms and molecules). Since the ratio of $m_m/m_e$ is very high, the electron temperature in a low pressure plasma is extremely high (e.g. on the order of $10^4$ K). Because ions have roughly the same mass as the corresponding neutral atoms and molecules, they lose most of their kinetic energy in collisions with molecules. The ion temperature $T_i$ is therefore much lower than $T_e$ (in the range of 300-1000 K), and it is only slightly higher than the temperature of molecules $T_m (~ 300$ K) [64].

2.2.3 Polymers

The word polymer was derived from the classical Greek words “poly” meaning “many” and “mers” meaning “parts”. Simply stated, a polymer is a material whose molecules contain a very large number of smaller structural units called monomers linked by covalent bonds in any conceivable pattern, which makes polymers macromolecules. In certain cases it is more accurate to call the structural or repeat unit of the a monomer parts because monomers are eliminated from the simple monomeric unit during some polymerization process [65]. Certain polymers available in nature are protein cellulose, silk etc. while many others including polystyrene, polyethylene and nylon are produced only by synthetic routes.

2.2.4 Classification based upon different factors related to polymers

All polymers can be assigned to one of two groups based upon their processing characteristics or type of polymerization mechanism. More specific classification can be made on the basis of polymer structure. Such groupings are useful because they facilitate the discussion of properties [65].

<table>
<thead>
<tr>
<th>Thermal processing behavior</th>
<th>Thermoplastics, Thermosets.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerization mechanism</td>
<td>Addition (step growth), Condensation (chain growth)</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>Homochain (single, double, triple bonds along their backbone), Heterochain</td>
</tr>
<tr>
<td>Monomer arrangement</td>
<td>Copolymers (two different repeating units in their chain), Ter polymers (three chemically different repeating units)</td>
</tr>
<tr>
<td>Tacticity</td>
<td>Isotactic, Syndeotactic, Atactic</td>
</tr>
</tbody>
</table>

However, the most common way of classifying polymers is to separate them into three groups:
Chapter 2  Introduction and Characterization Techniques of Plasma Polymerized Thin Films

2.2 Polymers

![Network Structure](image)

- **Thermoplastics**: Molecules in a thermoplastic are held together by relatively weak intermolecular forces so that the material softens when exposed to heat and then return to its original condition when cooled. Thermoplastic polymers can be heat-softened in order to process into a desired form and then can be solidified by cooling. Most linear and slightly branched polymers are thermoplastic as shown in Fig.2.1 (a). All the major thermoplastics are produced by chain polymerization.

- **Thermosets**: A thermosetting plastic or thermoset, solidifies or sets irreversibly when heated. Thermosets cannot be reshaped by heating. Thermosets usually are 3-dimensional networked polymers as shown in Fig.2.1 (b) Thermosets are polymers whose individual chains have been chemically linked by covalent bonds during polymerizations or by subsequent chemical or thermal treatment during fabrication. These polymers possess a high degree of cross-linking between polymer chains, which restrict the motion of the chain and lead to a rigid material.

- **Elastomers**: The polymer chain still have some freedom to move, but are prevented from permanently moving relative to each other by the cross-links. To stretch, the polymer chain must not be part of a rigid solid either a glass or a crystal. An Elastomer must be above its glass transition temperature $T_g$ and have a low degree of crystallinity.

2.2.5 Crystalline and amorphous states of polymer

Usually the biggest in polymer properties result from how the atoms and chains are linked together in space. Polymers that have a 1D structure will have different properties than...
those that have either a 2D or 3D structure. Thus polymers can also be classified in the following way [67].

<table>
<thead>
<tr>
<th>Form of network</th>
<th>Form of molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>One dimensional</td>
</tr>
<tr>
<td>Amorphous/irregular</td>
<td>Flexible chain</td>
</tr>
<tr>
<td>Rigid chain</td>
<td>Glassy plastics e.g. Polystyrene</td>
</tr>
<tr>
<td>Partial disoriented</td>
<td>Tough plastics e.g. Nylon</td>
</tr>
<tr>
<td>Partial oriented</td>
<td>Fibers and films (natural made)</td>
</tr>
<tr>
<td>Perfect</td>
<td>Single crystals e.g. Polyethylene</td>
</tr>
</tbody>
</table>

**i. Crystalline polymer:**
An important feature of crystalline polymer is that they consist not only of crystalline but amorphous regions as well. As a matter of fact, the crystalline and amorphous regions are separated by portions with an intermediate degree of ordering. As a rule there is no sharp borderline between the crystalline and amorphous regions. This is associated not to a small degree with the fact that one macromolecule may run through several crystallite and amorphous regions. This existence of such two phase chains is a characteristic feature of crystalline polymers. It is sometimes believed that a crystalline polymer may be regarded as an amorphous matrix in which small crystallites are randomly distributed. Obviously, such a model is unsuitable for highly crystalline polymers in which the crystallinity is 70 to 90%. It will be more natural to treat a crystalline polymer as a certain (sufficiently imperfect) crystalline lattice in which the voids are filled with amorphous matter.

**ii. Amorphous polymer:**
It has long been thought that amorphous polymers are aggregates of randomly entangled molecules. The concept of molecular felt was developed, which was assumed to correspond to the structure of an amorphous polymer. On the basis of X-ray studies it may be concluded that in amorphous polymers there are regions of short range order in which a single type of spatial type of orderliness is retained at a distance of $10^{15}$ Å from any point. Kargin, Kitaigorodsky and Slonimsky proposed a model for the structure of an amorphous polymer which states that two types of supermolecular structure are possible in amorphous polymers. It may consist either of globules formed by folded polymer molecules or of extended chains
which form bundles. It was supposed that the bundle length is much longer than the length of the macromolecules that make up the bundle. It was further assumed that bundles may display a certain flexibility and, as a result of this, there can occur the unfolding of the bundle regions inside which the chains are twisted into helices, or the concerted rotations of one portion of the bundle relative to another about the C-C bonds. An amorphous solid is formed when the chains have little orientation throughout the bulk polymer. The glass transition temperature is the point at which the polymer hardens into an amorphous solid. This term is used because the amorphous solid has properties similar to glass [67].

2.2.6 Process of plasma polymerization

Plasma polymerization is a procedure, in which gaseous monomers, simulated through plasma, condense on freely selectable substrates as high cross-linked layers. Condition for this process is the presence of chain producing atoms, such as carbon, silicium or sulfur in the working gas. In this process monomer gas is pumped into a vacuum chamber where it is polymerized by plasma to form a thin, clear coating. The monomer starts out as a liquid. It is converted to a gas in an evaporator and is pumped into a vacuum chamber. A glow discharge initiates polymerization.

Historically, proposed mechanisms of plasma polymerization have been based on conventional chain growth polymerization, such as free radical or ionic polymerization. In conventional chain growth polymerization, an initiating species reacts with monomer, and this process continues with the subsequent addition of monomer, proceeding until the reaction is terminated by processes such as disproportionation, combination, or transfer of reactive agents to some species separate from the polymer chain.

Chain growth polymerization is a molecular process that can proceed at low (atmospheric) pressure with catalysts, or spontaneously at high pressures without catalysts, or in the liquid
phase under a variety of conditions. The resultant polymer has a regular, repeating structure based on the monomer.

Vacuum deposition polymerization is an "atomic" process which yields a highly crosslinked product with a random structure, and vacuum conditions make gas phase chain growth a highly improbable growth mechanism due to thermodynamic constraints. Vacuum deposition processes, such as Parylene polymerization and plasma polymerization, occurs due to the dissociation of covalent bonds in gas phase molecules, and subsequent reactions between gas phase species and surfaces result in the deposition of polymeric materials. Dissociation results from interactions between monomer and energetic species, such as ions, electrons, photons, and excited neutrals.

In parylene polymerization, bond dissociation is due to thermolysis of monomer. The term monomer is not used in the same sense as in conventional polymerization. In vacuum deposition, the term monomer refers to any compound which can be used to deposit a film of polymeric material. Such compounds include but are not limited to those used in conventional polymerization. For example, plasma polymers can be obtained from methane, benzene, and saturated fluorocarbons.

Fig.2.4. Energy situation during plasma polymerization
By atomic process, it is meant that the species which contribute to growth are not well defined structures. Rather, they are created by fragmentation or rearrangement of the original monomer [68]. The energetic species can cause considerable fragmentation of the original monomer. The ionized species formed acquires energies typically of 0-2 eV, while electrons and metastables can achieve energies up to 20 eV. The processes that simultaneously occur during the plasma reaction are ionization, neutralization, recombination, polymerisation, etching, implantation, mixing and deposition. Under appropriate conditions an over layer will be formed on a solid substrate introduced into the reactor. The over layer will be formed where deposition is kinetically dominant over etching, ion implantation and atomic mixing.

![Fig.2.5 Competitive ablation and polymerization scheme of glow discharge polymerization.](image)

Plasma polymerization is characterized by several features:

1. Plasma polymers are not characterized by repeating units, as is typical for conventional polymers.
2. The properties of the plasma polymer are not determined by the monomer being used but rather by the plasma parameters.
3. The monomer used for plasma polymerization does not have to contain a functional
group, such as a double bond [3].
The significant advantages of depositing thin films via plasma polymerization include: [69]
1) The starting material does not have to contain the type of functional groups normally
associated with conventional polymerization.
2) Plasma polymerized films are often highly adherent to a variety of substrates.
3) Deposition is achieved without the use of solvents (environmentally benign process).
4) The thickness of plasma polymerized films can be easily varied from 2 nm to $10^6$ nm.
5) Through careful control of the plasma polymerization parameters, plasma polymer films
can be tailored to contain specific functional groups.
6) Plasma polymerized films can be deposited directly onto an activated substrate without
breaking vacuum.

2.2.7 Glow discharge

A glow discharge is a kind of plasma. It is an ionized gas consisting of equal concentrations of
positive and negative charges and a large number of neutral species i.e. a plasma. In the
simplest case, it is formed by applying a potential difference (of a few 100 V to a few kV)
between two electrodes that are inserted in a cell (or that form the walls of the cell). The cell is
filled with a gas (an inert gas or a reactive gas) at a pressure ranging from a few m Torr to
atmospheric pressure. Due to the potential difference, electrons that are emitted from the
cathode, give rise to collisions with the gas atoms or molecules (excitation, ionization,
dissociation). The excitation collisions give rise to excited species, which can decay to

Fig.2.6 Schematic representation of the basic processes in a glow discharge.
lower levels by the emission of light. This process is responsible for the characteristic name of the “glow discharge”. The ionisation collisions create ion-electron pairs. The ions are accelerated toward the cathode, where they release secondary electrons. These electrons are accelerated away from the cathode and can give rise to more ionization collisions. In its simplest way, the combination of secondary electron emission at the cathode and ionization in the gas, gives rise to self-sustained plasma. The character of the gas discharge critically depends on the frequency or modulation of the current.

2.2.8 Control parameters of plasma polymer thin film properties

Typically plasma polymerization reaction occurs at a pressure of 1.33 to 1.33×10^2 Pascal. The gas phase reaction involving polymerization process can be explained by a modified kinetic theory of the gas. The process of plasma polymerization involves the fragmentation of the monomer into reactive species and recombination of the fragments on a substrate which is placed inside the plasma chamber. The following kinetic and mechanistic parameters are to be considered when the polymerization of a monomer is carried out.

(A). Monomer: The monomer most commonly used for plasma polymerization are:
   1. Hydrocarbons: Consisting of triple, double, cyclic structure and saturated monomers. Also the polar group containing hydrocarbons.
   2. Fluorocarbons
   3. Silicon containing monomers
   4. Volatile organometallic compounds

(B). Generation of glow discharge:
   1. DC glow discharge
   2. DC glow discharge of alternating polarity (at low frequencies e.g. 60 Hz or <500 kHz).
   3. AC glow discharge
   4. RF (13.56 MHz) glow discharge
   5. Microwave (300 MHz to 10 GHz) glow discharge
   6. Pulsed glow discharge
   7. Atmospheric pressure glow discharge
   8. Dielectric barrier glow discharge

Depending on the reactor geometry there are several types of discharges:
   1. Capacitively coupled plasmas
   2. Inductively coupled plasmas

(C). Effect of physical plasma process parameters:

1. Frequency of exciting potential excitation power,
2. excitation power $W$,
3. monomer(s) flow rate $F$ [Volume(STP)/unit time],
4. Plasma pressure $P_g$,
5. Geometrical factors, e.g. location of monomer inlet and to exciting electrodes, dimensions of reactor vessel and of electrodes, etc.,
6. Temperature of deposition site.

The effect of these parameters can be understood by considering there effect on basic plasma parameters i.e. electron density $n_e$, electron energy distribution $f(E)$, gas density $N_g$, residence time for a gas molecule in plasma, $\tau_p$.

Yasuda proposed a controlling parameter, $W/FM$ which is an apparent input energy per the unit of monomer molecule in J/kg; therefore, the magnitude of the $W/FM$ parameter is considered to be proportional to the concentration of activated species in plasma. Depending on this parameter, the rate of formation of polymer; increases or decreases under certain conditions [3].

2.2.9 Overall reactions and growth mechanism in plasma polymerization

In plasma; monomer molecules gain high energy from electrons, ions, and radicals and are fragmented into activated small fragments, in some cases into atoms. These activated fragments are recombined sometimes accompanying rearrangement, and the molecules grow to large- molecular-weight ones in a gas phase or at the surface of substrates. The repetition of activation, fragmentation, and recombination leads to polymer formation. The chemical structure of polymers formed by plasma polymerization, if the same monomer (which is used in conventional polymerization) was used, is never predicted from the structure of the monomer, because the fragmentation and rearrangement of the monomers occur in the plasma [69].

Plasma polymerization consists of several reaction steps:

At first, generation of free radicals and atoms are occurred by collisions of electrons and ions with monomer molecules, or by dissociation of monomers absorbed on the surface of the sample. Secondly, propagation of the formation of polymeric chain which can take place both in the gas phase (by adding radical atoms to other radicals or molecules) and on the deposited polymer film (by interaction of the surface free radicals with either gas phase or
absorbed monomers). Finally, termination can also take place in the gas phase or at the polymer surface, by similar process as in the propagation step, but ending either with the final product or with a closed polymer chain. The individual steps and reaction that occur in plasma polymerization generally depends on the system. This type of polymerization can be represented by the following statements.

Initiation or Reinitiation

\[ M_i \rightarrow M_i^* \]
\[ M_k \rightarrow M_k^* \]

Propagation and Termination

\[ M_i^* + M_k^* \rightarrow M_i M_k \]
\[ M_i^* + M_k \rightarrow M_i M_k \]

In which \( i \) and \( k \) are the numbers of repeating units (i.e., \( i=k=1 \) for the starting material), and \( M^* \) represents a reactive species, which can be ion of either charge, an excited molecule, or a free radical produced by \( M \) but not necessarily retaining the molecular structure of the starting material. In plasma state polymerization the polymer is formed by the repeated stepwise reaction.

Fig. 2.7 Schematic representation of bicyclic step-growth mechanism in plasma polymerization.

Yasuda suggested that the growth mechanism of plasma polymerization would vary likely be the rapid step growth reaction,

\[ [ M_m^* + M_n^* \rightarrow M_{m+n} ] \times N \]
Where $M^*$ is the mono functional reactive species such as a free radical $R^*$, $N$ is the number of repetitions of similar reactions and $m$ and $n$ represents different reactive species.

In case of monofunctional reactive species, a single elementary step is indeed a termination process and does not contribute without additional elementary step.

For a difunctional reactive species, such as a diradical, the polymerization can be represented by

$$N^r M^* \rightarrow ^r(M_n)^*$$

It shows that as polymerized polymers contain a measurable quantity of free radicals.

The overall polymerization mechanism based on the rapid step growth principle is shown in Fig.2.6. Where $M_x$ refers to a neutral species, $M^*$ is the monofunctional activated species and $^r M^*$ is the difunctional. The subscripts $i, j, k$ indicate the difference in the size of species involved. Cycle I is via the repeated activation of the reaction products from monofunctional activated species, and cycle II is that of difunctional. The species participating in the rapid step growth polymerization can be mono or multifunctional (radical, cation, cation-radical, diradical, etc.) [4].

2.2.10 Film structure

In most cases plasma polymers are cross-linked and have a disordered structure. Structural preservation and cross-linking gradients can be controlled through process parameters, such as pressure, working gas-flow and applied electrical output; so one can also construct so-called gradient layers; i.e with increasing degree of cross-linking over thickness.

Special layer characteristics those are qualified for a multitude of applications:

- excellent coating adhesion on almost all substrates
- chemical, mechanical and thermal stability
- high barrier effect

2.2.11 General properties of plasma polymers

1. Plasma polymerized films are thin (from hundreds of angstrom to several microns) and pinhole-free.

2. Plasma polymerized films are insoluble in conventional organic solvents, indicating the highly cross-linked nature of the polymer.

3. The differential scanning chalorimetry and differential thermogravimetric analyses have been used by several authors to show that plasma derived polymers have no phase transitions until decomposition occurs. They have remarkable thermal stability for
example, 80 wt % of a film prepared from methyl chloride remains at 800 °C and 40 wt % of a styrene derived films remains at 700 °C.

4. Plasma derived films have a mesh structure, with only short chain segments between branched and cross-linked points. Its structure generally contains numerous unsaturated groups, aromatic groups and side branches.

5. There are existences of trapped free radicals in plasma derived films. These active sites are probably formed both through incorporation of free radicals from the gas phase and by the impingement of active plasma species and radiation onto the depositing film. Due to the highly cross-linked structure, trapped have low mobility and do not recombine rapidly. Upon exposure to the atmosphere, these trapped radicals react with O [1].

6. Plasma polymerized thin organic films are, in general, dielectric materials with insulating properties and extremely low conductivities.

2.2.12 Some characteristic differences of plasma polymers from conventional polymers

1. Plasma polymers have a higher elastic modulus than the conventional polymers. (May be due to dense cross-linkage of polymer).

2. Low water vapor or gas permeability and low decay of waitability than the conventional polymers (due to cross-linking).

3. The properties of plasma polymers are much more dependent on the processing factors and morphology than the conventional polymers. For example, properties of plasma polymers are directly or indirectly related to the number of free radicals.

4. Internal stress in plasma polymer is a characteristic property which is not found in most conventional polymers.

5. Solvent resistance of plasma polymers is generally higher than the conventional polymers.

6. The surface energies of plasma polymers of hydrocarbons are generally higher than those of conventional hydrocarbon polymers due to the presence of O containing groups.

2.2.13 Advantages and disadvantages of plasma polymerization

The deposition of thin films on solid substrates by the plasma polymerization process has been practiced for over two decades. The plasma polymerization of simple organic monomers (i.e. hydrocarbons or silanes) produces films that are highly cross-linked, pinholefree, thermally and chemically stable, and very adherent. Furthermore, plasma polymerized films can be prepared from monomers that cannot be polymerized by
conventional chemical techniques (i.e. methane, ethane, saturated hydrocarbons, organo-metallics). The characteristics of the plasma-formed films (adhesion, mechanical properties, extent of crosslinking, etc.) are dictated by the choice of kinetic formation parameters such as RF power input, plasma pressure, and reaction time. The significant advantages of depositing thin films via plasma polymerization include:

1) The most significant advantage of plasma polymerization is its ability to produce polymer films of organic compounds that do not polymerize under normal chemical polymerization conditions. Nearly all monomers, even saturated hydrocarbons and organic compounds without a polymerizable structure such as a double bond, can be polymerized with this technique.
2) Plasma polymerized films are often highly adherent to a variety of substrates.
3) Deposition is achieved without the use of solvents.
4) The thickness of plasma polymerized films can be easily varied from 2 nm to 1000 nm.
5) Through careful control of the plasma polymerization parameters, plasma polymerized films can be tailored to contain specific functional groups.
6) Plasma polymerized films can be deposited directly onto an activated substrate without breaking vacuum.
7) In the surface modification plasma polymerization is limited to the top surface layer and does not affect the bulk properties of the polymer.
8) The modification by plasma processes is largely independent on the structure or chemical reactivity of the substrate.
9) A broad range of functional groups can be introduced at the surface, by variation of the gas that is used. In general, the modification is fairly uniform over the whole substrate.
10) The plasma treatment or polymerization is a simple one-step procedure, and is an all-dry process.

Some of the disadvantages inherent to plasma processes are summarized in the following list:

1) A vacuum system is required for plasma treatments. This demand increases the cost of the operation.
2) Due to the complexity of plasma processes, it is not easy to achieve a good control over the chemical composition of the surface after modification. The influence of process parameters such as reactor geometry, input power, and gas flow on the chemical composition of the modified material should be investigated separately to find the optimal treatment conditions for each gas.
3) The main drawback in this case is related to the presence of the energetic species in the plasma which dissociate the precursors and so the obtained materials contains only in a small extent the original bonding environment. Therefore the challenge in using plasma polymerization for obtaining conductive polymers is to find proper configurations and deposition conditions to preserve the conjugated double bonds. [5]

2.2.14 Types of reactors

There are a few designs for apparatus used in plasma polymerization, one of which is the Bell (static type), in which monomer gas is put into the reaction chamber, but does not flow through the chamber. It comes in and polymerizes without removal. This type of reactor is shown in Fig.2.8 (a). This reactor has internal electrodes, and polymerization generally takes place on the cathode side. All devices contain the thermostatic bath, which is used to regulate temperature, and a vacuum to regulate pressure.

A great number of deposition systems using low pressure plasma was described in the literature. Generally the three types of plasma polymerization deposition systems (reactors) can be distinguished as pointed out by Shi: (i) internal electrode reactors (Fig. 2.8 (a)) (ii) external electrode reactors (Fig. 2.7 (b)) and (iii) electrodeless microwave or high frequency reactors (Fig. 2.8 (c)).

The leading configuration in the group (i) is a bell-jer type reactor with internal parallel plate electrode arrangement. The discharge can be excited either by DC or AC and/or RF voltage. DC is used in special cases or in the case where a planer magnetron is used. The magnetron electrode is serves as a cathode and is at high negative potential (several hundred volts) whereas the counter electrode serves as an anode and is usually connected to the steel-bell-jar and the earthed (asymmetrical arrangement). The anode (substrate holder) may be also isolated and in this case biased.

For a plasma polymerization process, more typical is the discharge excitation by AC and RF voltages in so called symmetrical arrangement. If the frequency of the excitation voltage is above about 50 kHz (100 kHz) the power must be delivered through a matching unit and determined by a power meter. In case of the asymmetrical arrangement where the excitation DC negative bias is developed on this electrode. In this case the surface (target) of the excitation electrode is sputtered by positive ions (RF sputtering). In some processes this may be the reason for concern as there is a danger of impurities sputtered off from the excitation electrode. In other cases this may be welcome e.g. simultaneous plasma
Fig. 2.8 Glow discharge reactor (a) Bell Jar type capacitively coupled (internal electrode) (b) inductively coupled (external electrode) (c) Microwave plasma reactor (d) Schematic drawing of the symmetrical and asymmetrical plasma reactor and (f) Different inlet positions of glow discharge reactor.
polymerization and co-sputtering of the metallic target for composite metal/plasma polymer film deposition. External electrode reactors use ring electrodes or an external coil around a tube from glass or silica RF power may be coupled into the plasma inductively but in most cases the coupling is of a capacitive nature. Therefore when the external coil is used instead of the term indicative coupling one could use inductive excitation to point out the use of the coil but to avoid the confusion as the coupling is likely capacitive. The reactor then cannot be considered as electrodeless as the DC negative bias appears on the inner electrode wall under the coil turn or under the ring electrode. The substrate is positioned inside the plasma or downstream of the plasma. Electrodeless microwave reactors are usually composed from a silica tube that passes through the resonant cavity coupled to a microwave power supply (typically 2.45 GHz). Plasma is generated in the tube within the cavity and substrates are positioned downstream of the plasma. The cavity actually acts instead of the RF excitation coil or ring electrodes [66].

Another popular reactor type is the flow through reactor (continuous flow reactor), which also has internal electrodes, but this reactor allows monomer gas to flow through the reaction chamber as its name implies, which should give a more even coating for polymer film deposition. It has the advantage that more monomer keeps flowing into the reactor in order to deposit more polymer. It has the disadvantage of forming what is called “tail flame,” which is when polymerization extends into the vacuum line.

Atmospheric-pressure plasma system is also growing in popularity, which is useful for depositing thin polymer films. This system bypasses the requirements for special hardware involving vacuums, which then makes it favorable for integrated industrial use. It has been shown that polymers formed at atmospheric-pressure can have similar properties for coatings as those found in the low-pressure systems.

### 2.2.15 Doping of plasma polymers and formation of charge transfer complex

The modified thin films of pure and doped polymers are quite important for various engineering and technological purposes because doping of polymers causes changes in the structure and, therefore, in the chemical and physical properties. Plasma polymerized organic thin films are generally poor electronic conductors or insulators, due to a low concentration of free charge carriers in the pristine state. Upon doping the polymer, mobile charge carriers are generated and the conductivity can be modified from as low as $10^{-10}$ to
Doping can be made in different ways, where chemical and electrochemical doping are commonly used [28, 47].

Iodine is referred as an electron acceptor and a potential doping agent with different polymers in many charge transfer complexion studies. It has been reported that as, iodine possess a low molecular orbital with an ionization potential of 7.8 eV and significant electron affinity, they capture a weakly localized π-electron of polymer macromolecule and forms a charge-transfer complex. A charge-transfer complex or electron-donor-acceptor complex is an association of two or more molecules, or of different parts of one very large molecule, in which a fraction of electronic charge is transferred between the molecular entities, alike of Van der Waals interaction. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. The nature of the attraction in a charge-transfer complex is not a stable chemical bond and is thus much weaker than covalent forces. The attraction is created by an electronic transition into an excited electronic state, and is best characterized as a weak electron resonance in the visible region of the electro-magnetic spectrum which is often referred to as charge transfer bands. Charge transfer interactions occur between all available donor orbital and all available acceptor orbital. The total stabilization resulting from charge transfer interaction is the sum of the individual contributions from all possible combinations of donor and acceptor orbital.

2.2.16 Applications of plasma polymerized films

Plasma polymerized films are gaining recognition as a potential material in diverse scientific application areas. Some of them are cited as follows [81]:

i. Electronics:
IC, VLSI resist, amorphous semiconductor and amorphous fine ceramic etching.

ii. Electrets:
Thin film dielectrics, insulator, and separation membrane for batteries.

iii. Chemical processing:
Reverse osmosis membrane, permselective membrane, water vapor barrier, gas separation membrane-lubrication and insolubilization.

iv. Surface modification:
Adhesion and compatibility improvements, coating, anti-crazing and scratching.

v. Optical:
Anti-reflection coating, anti-dimming coating, improvement of transparency, refractive index controlling, optical fiber, optical wave guide laser and optical window, contact lens and prism etc.

**vi. Textile:**
Anti-flammability, anti-electrostatic treatment, dyeing affinity, hydrophilic improvement, water repellence, shrink-proofing, etc.

**vii. Biomedical:**
Immobilized enzymes, organelles and cells, sustained release of drugs and pesticides, sterilizations and pasteurization, artificial kidney, blood vessel, blood bag, anti-clotting.

### 2.3 Characterization Techniques of Plasma Polymerized Thin Films

#### 2.3.1 Introduction

Plasma polymerized organic conjugated polymer thin films have received great attention in recent years for their optical response by delocalized electrons which yielded potentials for applications encompassing optoelectronic devices like light-emitting devices, photodiodes, sensors, light guide materials, coatings, etc. [70-72].

Plasma polymer is a good candidate in the field of surface coating and sensor technology. From the implicational point of view it is important to analyze the thermal stability of a plasma polymer. Polymers with highly aromatic structures are generally considered as a successful applicant for use at high temperatures for extended periods of time [67]. To determine the thermo-physical properties several methods are commonly used: differential thermal analysis (DTA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The use of SEM can be found in numerous investigations dealing with the surface morphology of different polymer materials. In the case of plasma polymer the main interest is to find a homogeneous, dense, without pinhole thin films which are useful as corrosion protective coatings for microelectronic devices and selective layers in sensors. [44, 72, 73]

It is rarely, if ever, possible to identify an unknown compound by using FTIR spectroscopy alone. Its principal strengths are: (i) it is a quick and relatively cheap spectroscopic technique, (ii) it is useful for identifying certain functional groups in molecules and (iii) an FTIR spectrum of a given compound is unique and can therefore serve as a fingerprint for this compound. Researchers apply this technique enormously because it involves collecting absorption information and analyzing it in the form of a spectrum [3, 73-77].
To investigate the optically induced electronic transitions, band structure and the energy band gap of both crystalline and amorphous materials the nature of optical absorption near the absorption edge is very important. Usually, the steepness of the optical absorption edge in the amorphous material is very much dependent on the localization of some states in the energy gap resulting from the chemical impurities, vacancies, and broken and dangling bonds [76]. For plasma polymerized thin films, ultraviolet visible (UV-vis) spectroscopic method is being widely used by many investigators to determine the presence, nature and extent of conjugation in materials, impurity states, optical energy gaps due to direct and indirect transitions, extinction coefficient, etc. [7-18].

Modern life style increasingly demands more from the polymers than their traditional role of insulators for heat and electric current. To satisfy this purpose much more attentions have been made in the research activities to investigate the electrical responses of the polymer insulators. In recent years, plasma polymerized organic thin films have a growing interest to study as active components widely used in fabricating thin film devices like dielectric [30] and functional layers for electronic functional elements in thin film transistors, diodes, switching elements, photovoltaic devices, capacitors, sensors [13, 31, 50] etc. Knowledge of the conduction mechanism in the polymer thin film is one of the most essential factors for its applications in their respective fields. The electrical transport properties in the plasma polymerized organic thin films can be modified significantly by introducing charge carriers in the form of extra electrons and/or holes. In this regard iodine plays a significant role as a doping agent in various plasma polymerized thin films [12, 16, 30, 51].

The dielectric behavior of polymer films is of considerable interest due to their applications for insulation, isolation and microelectronics. The dielectric constant and the loss factors are the most convenient and sensitive methods for studying the dielectric behavior of polymer. The plasma polymer contains a certain quantity of polar groups whether the monomer used was polar or nonpolar. The presence of polar groups is without doubt a significant reason for different dielectric behavior than the conventional polymers. Another possible reason for their different dielectric behavior is their very small thickness because the bulk properties of materials are influenced by their surface properties [4].

A brief discussion on the characterizing techniques which are useful to ascertain the general properties of plasma polymers are stated below.
2.3.2 Thermal Analyses

Thermal analysis is used to establish thermodynamic properties which are essential for understanding the behavior of material under different heating and cooling rates, under inert, reduction or oxidation atmosphere or under different gas pressures. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured to a controlled temperature program [77]. The thermal behavior of polymers typically related to the melting of crystalline domains, the glass transition behavior, flammability, and thermal stability. Flammability and thermal stability refer to chemical transformations. Melting and glass transition are due to changes in the morphology and relaxation behavior of the polymer.

2.3.2.1 Instrumentation

A technique in which the difference in temperature between the sample and a reference material is monitored against time or temperature, while the sample and reference material are subjected to the same controlled temperature programme. Fig.2.9 shows the block diagram of DTA. The sample and the reference are placed symmetrically in the furnace. The furnace is controlled under a temperature program and the temperature of the sample and the reference are changed. During this process, a differential thermocouple is set up to detect the temperature difference between the sample and the reference. Also, the sample temperature is detected from the thermocouple on the sample side.

![Fig.2.9 Block diagram of a DTA instrument](image)

TG is a technique that measures mass change in a sample, and it is used to detect evaporation, decomposition, oxidation and other effects of temperature change that cause
mass changes. Fig.2.10 shows the balance beams for the sample and the reference are located in the furnace. The masses of the sample and the reference are measured by the sensitivity-calibrated drive coils separately. The mass difference is sent as TG signal. By the differential mass measurement, the effects of the beam expansion, the convection flow, and buoyant force are cancelled. Thus the highly sensitive thermogravimetry measurement is achieved. The mass measurement of the sample and the reference by the independent drive coils enables the easy adjustment of the TG baseline drift electrically. Also, thermocouple is located in each holder which enables the simultaneous DTA signal output. TG can be utilized for the analysis of the thermal decomposition, the oxidization, the dehydration, the heat resistance, and kinetics analysis. By combining with the other measurement technique, variety of information can be achieved from one sample. In particular, TG/DTA simultaneous measurement instrument is most common.

![Block diagram of a horizontal differential TG instrument.](image)

In a DSC, there are two pans isolated from the ambient environment in a chamber. One pan contains the sample to be analyzed, and the other pan is empty and is used as a reference pan. Both pans have heaters underneath them that are used to raise or lower the temperature. Each pan also has a sensor that indicates what the temperatures of the pans are at any given moment. Using computer controlled sensors and logic, the heaters are set to heat the pans at a constant rate ($\Delta T/\Delta t$), that is the rate of temperature change is the same, for example 5 degrees Celsius per minute. The instrumentation is also designed to ensure that the pans heat at the same rate as each other. Having the pans heat at a constant rate, but also the same rate as each other might seem repetitious; however the heat flow, which is the rate at which thermal energy ($\Delta Q/\Delta t$) is supplied to the pans, does differ, due to the fact that there is material in one of the pans, and nothing in the other pan. Consider, for example, two pots, one with water and one empty, and both pots start out at the same initial temperature and are
then placed on stoves. If each pot is heated at the same rate (both stove settings are placed on low, for example) the pot with the water in it will heat up slower, that is the rate of temperature change will be smaller than the pot with nothing. This is because heat capacity is different for water than it is for air. The same thing happens in the pans of the instrument

![Diagram of DSC instrument](image)

**Fig. 2.11** Block diagram of a DSC instrument.

i.e. the pan with the material/sample in it will heat up slower than the reference pan which contains nothing. Going back to the example of the two pots, the computer would control the stoves and set the pots to be heated at a constant 5 degrees per minute, and also monitor the temperature of each pot and ensure that the two pots heat at the same rate. Since the pot with the water in it will heat up slower than the empty pot, the computer will have to supply a higher heat flow to the pot containing water in order to force the pots to heat at the same rate. The computer keeps track of the starting temperature, heating rate and heat flow, and records the difference in heat flow between the reference pan and the sample pan (water pot as the example), which is the heat flow for the sample, and plots it against temperature. The DSC experiment is all about the measurement of how much heat that the sample pan heater has to put out as compared to the reference pan heater.

### 2.3.2.2 Principle of Thermogravimetric, Differential Thermal and Differential Scanning Calorimetric analyses

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, or against temperature. Changes in the sample which lead to the absorption or evolution of heat can be detected relative to the inert reference. Nevertheless, the DTA curves can record the transformations where the heat
is either absorbed or released (dehydration, decarbonation, burning of materials, ordering etc.). The principle of the "classical" arrangement is readily explained with reference to the figures in Fig.2.12.

S and R are containers holding the sample and an inert reference material. In these are thermocouples measuring their respective temperatures. By connecting the thermocouples in opposition, the difference in temperature (ΔT) is also measured. If S and R are heated at the same rate, by placing them in the same furnace, their temperatures will rise as in the middle figure. TR rises steadily, as the reference material is chosen to have no physical or chemical transitions. TS also rises steadily in the absence of any transitions, but if for instance the sample melts, its temperature will lag behind TR as it absorbs the heat energy necessary for melting. When melting is complete, steady heating is resumed. The right-hand figure shows the DTA curve- a plot of ΔT against time or more usually, sample temperature. The curve shows an endothermic (heat-absorbing) peak. If an exothermic (heat-producing) event had occurred, the curve would show a peak in the opposite direction. The area A on the curve is proportional to the heat of the reaction:

$$\Delta H = kT_A = k\int \Delta T \, dt$$  \hspace{1cm} (2.4)

The constant $k$ comprises many factors, including the thermal properties of the sample and varies with temperature.

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Thermogravimetric analysis (TGA) is used
to determine a material’s thermal stability and its fraction of volatile components by monitoring the weight change that occurs as a specimen is heated.

The thermogravimetric analysis has very versatile application in polymer analysis. The acquired information by TGA is confined to the detection of change in mass of the sample as its temperature or time duration alters. The technique is used to study the decomposition, oxidation reactions and also some physical processes such as vaporization, sublimation and desorption. The main conclusions drawn by TGA are: thermal stability, compositional analysis, life time assessment and degradation kinetics. The TG curve provides information about the decomposition of various polymers, which may be used for identification purposes and also assessment of thermal stability. The basic route by which a polymer degrades can be categorized by main chain scission, side chain scission, elimination, depolymerization. Principle uses of TGA include measurement of a material’s thermal stability and its composition. Typical applications include:

- Filler content of polymer resins
- Residual solvent content
- Carbon black content
- Decomposition temperature
- Moisture content of organic and inorganic materials
- Plasticizer content of polymers
- Oxidative stability
- Performance of stabilizers
- Low molecular weight monomers in polymers

In thermogravimetry a continuous graph of mass change against temperature is obtained when a substance is heated at a uniform rate or kept at constant temperature. A plot of mass change versus temperature ($T$) is referred to as the thermogravimetric curve (TG curve). For the TG curve, mass ($m$) decreasing downwards on the y axis (ordinate), and temperature ($T$) increasing to the right on the x axis (abscissa) are generally plotted as illustrated in Fig.2.12. Sometime time ($t$) in place of $T$ is also can be plotted.

In a TG curve of a single stage decomposition, there are two characteristic temperatures; the initial $T_{in}$ and the final temperature $T_{fi}$ (see Fig.2.13). $T_{in}$ is defined as the lowest temperature at which the onset of a mass change can be detected by thermo balance operating under particular conditions and $T_{fi}$ as the final temperature at which the particular decomposition appear to be complete. Although $T_{in}$ has no fundamental significance, it can
still be a useful characteristic of a TG curve and the term procedural decomposition temperature has been suggested. The difference $T_{fi} - T_{in}$ is termed as reaction interval. In a dynamic thermogravimetry a sample is subjected to continuous increase in temperature usually linear with time whereas in isothermal or static thermogravimetry the sample is maintained at a constant temperature for a period of time during which any change in mass is noted [78].

\[
\text{Fig.2.13 A typical TG curve.}
\]

Differential scanning calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert material such as alumina, or just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate. Since the DSC is at constant pressure, heat flow is equivalent to enthalpy changes:

\[
\left( \frac{dq}{dt} \right)_p = \left( \frac{dH}{dt} \right) \\
\text{(2.5)}
\]

Here $dH/dt$ is the heat flow measured in mcal sec$^{-1}$. The heat flow difference between the sample and the reference is:

\[
\Delta \frac{dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}} \\
\text{(2.6)}
\]

and can be either positive or negative. In an endothermic process, such as most phase transitions, heat is absorbed and, therefore, heat flow to the sample is higher than that to the reference. Hence $\Delta dH/dt$ is positive.
The calorimeter consists of a sample holder and a reference holder. Both are constructed of platinum to allow high temperature operation. Under each holder is a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. The difference in the power to the two holders, necessary to maintain the holders at the same temperature, is used to calculate $\frac{\Delta dH}{dt}$. A flow of $N_2$ is maintained over the samples to create a reproducible and dry atmosphere. The $N_2$ atmosphere also eliminates air oxidation of the samples at high temperatures. The sample is sealed into a small aluminum pan. The reference is usually an empty pan and cover. The pans hold up to about 10 mg of material.

A special case in which the temperature of a phase transformation is of great importance in polymers is the glass transition temperature, $T_g$. This is the temperature at which amorphous polymers are converted from a brittle, glasslike form to a rubbery, flexible form. This is not a true phase transition but one that involves a change in the local degrees of freedom. Above the glass transition temperature certain segmental motions of the polymer are comparatively unhindered by the interaction with neighboring chains. Below the glass transition temperature, such motions are hindered greatly and the relaxation times associated with such hindered motions are usually long compared to the duration of the experiment.

In DSC experiments the data of temperature increase ($T$) are plotted against the difference in heat output of the two heaters at a given temperature. Mathematically, the computer will provide plots of the difference in heat output of the two heaters against temperature. This means that the above plot is the heat absorbed by the polymer against temperature.

Heat / time $= H/\tau = \text{heat flow}$

Temperature increase / time $= \Delta T/\tau = \text{heating rate}$

Then the heat capacity is:

$$C_p = \frac{(H/\tau)}{\Delta T/\tau} = \frac{H}{\Delta T} \quad (2.7)$$

The amount of heat it takes to get a certain temperature increase in a material is called heat capacity, or $C_p$. A typical DSC plot of a polymer will look like of Fig. 2.14 (a). It is important to recognize that not all polymers will show $T_c$ and $T_m$. $T_m$ and $T_c$ will only show up for polymers that can form crystals. Completely amorphous polymers exhibit only $T_g$. However, polymers with both crystalline and amorphous domains, will show all the features as shown in Fig 2.14(a). The $T_g$ can be detected according to the Fig. 2.14 (b). If there are sloping baselines before and after the glass transition, extrapolating the baselines forwards and backwards (as shown by dotted lines) and taking the baseline shift the start and end points of $T_g$ can be determined. The $\Delta C_p$ of $T_g$ can be measured by subtracting the
heat flow at the two $T_g$ points. The units of the heat flow are mcal sec$^{-1}$ and the temperature scan rate is usually expressed as °C min$^{-1}$. So to be consistent with units, 60 sec min$^{-1}$ should be multiplied according to the form:

$$\Delta C_p = \left(\frac{mcal}{sec}\right) \left(\frac{min}{°C}\right) \left(\frac{60sec}{min}\right)$$

### 2.2.3 Scanning Electron Microscopy

#### 2.2.3.1 Instrumentation

In SEM a beam of electrons is generated in the electron gun, located at the top of the column, which is pictured to the left. This beam is attracted through the anode, condensed by a condenser lens, and focused as a very fine point on the sample by the objective lens. The scan coils are energized (by varying the voltage produced by the scan generator) and
create a magnetic field which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the Cathode-ray tube (CRT) which produces a pattern of light deflected back and forth on the surface of the CRT. The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT. The electron beam hits the sample, producing secondary electrons and backscattered electrons from the sample. These electrons are collected by a secondary detector or a backscatter detector, converted to a voltage, and amplified. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot of light to change. The image consists of thousands of spots of varying intensity on the face of a CRT that correspond to the topography of the sample.

2.2.3.2 Theoretical background
At any given moment, the specimen is bombarded with electrons over a very small area; several things may happen to these electrons. They may be elastically reflected from the specimen, with no loss of energy or absorbed by the specimen and give rise to secondary electrons of very low energy, together with X-rays. They may be absorbed and give rise to the emission of visible light (an effect known as cathodoluminescence). And they may give
rise to electric currents within the specimen. All these effects can be used to produce an image. Secondary electron imaging is the most common because it can be used with almost any specimen. Moving electrons are not only moving particles, but also behave as waves; this is called in quantum mechanics “particle/wave duality”. Therefore, electrons obey all the optical laws of diffraction. If there are two small slits beside each other, on one side of the slit a small electron source and at the other side of the slit a fluorescent screen, if the electron were only particles, two illuminated lines would be seen on the screen. However, in reality the screen will show a large number of black and white lines, which is only due to the wave like nature of electrons. The wavelength of an electron is much smaller than that of visible light. Therefore, the electron microscope has a possibility of showing much smaller details. Small samples up to several millimeters and sometimes even larger can be investigated directly in the SEM if the sample material has a sufficiently high electric conductivity to prevent charging produced. For insulating samples, it needs to be coated with an extremely thin layer of an electrically conducting material (Ag, Au etc.).

2.2.4. Energy Dispersive X-ray analysis

EDX Analysis stands for ‘Energy Dispersive X-ray’ analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM) and can not operate on its own without the latter.

During EDX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms’
own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established.

The EDX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.

### 2.2.5 Fourier Transform Infrared Spectroscopy

The term "infrared" covers the range of the electromagnetic spectrum between 0.78 and 1000 μm. Band positions in IR spectra are presented either as wavenumbers or wavelengths. The wavenumber unit (cm⁻¹, reciprocal centimeters) is used most often since it is directly proportional to the energy of the vibration and since most modern instruments are linear in the cm⁻¹ scale. Wavelength is reported in micrometers (μm, 10⁻⁶ meters) although the order literature refers to this quantity as the micron (μ). Wavenumbers are reciprocally related to wavelength as follows.

\[
\text{cm}^{-1} = \frac{1}{\mu m} \times 10^4
\]  

(2.8)

It is useful to divide the infra red region into three sections; near, mid and far infra red. The most useful IR region lies between 4000 and 670 cm⁻¹.

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength range (μm)</th>
<th>Wavenumber range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.78 - 2.5</td>
<td>12800 - 4000</td>
</tr>
<tr>
<td>Middle</td>
<td>2.5 - 50</td>
<td>4000 - 200</td>
</tr>
<tr>
<td>Far</td>
<td>50 -1000</td>
<td>200 – 10</td>
</tr>
</tbody>
</table>
2.2.5.1 Instrumentation

In simple terms, FTIR spectra are obtained by detecting changes in transmittance (or absorption) intensity as a function of frequency. This instrument uses a source of infrared radiation such as a nichrome wire or cooled rod of silicon carbide to produce a range of frequencies which are then separated into individual frequencies using a monochromator diffraction grating. The beam produced is then split into two; and one passes through the sample whilst the other is used as a reference beam. The two beams then converge on the detector which measures the difference in intensity and then sends a proportional signal to the recorder. The resulting plot is a measure of transmission against frequency which is usually plotted as wavenumber (cm\(^{-1}\)). Most commercial instruments separate and measure FTIR radiation using dispersive spectrometers or Fourier transform spectrometers. This method has some obvious advantages. Firstly, it is much quicker, taking seconds instead of minutes to record a complete spectrum. A further advantage is that it is possible to get a spectrum from very small or very dilute samples by performing multiple scans and adding the data to improve the signal-to-noise ratio. Slow scans using diffraction gratings are inefficient.

2.2.5.2 Fourier transform infrared spectrometer

Almost all modern FTIR spectrometers use a different approach, the Fourier transform method, to scan the full spectral range at the same time.

A Fourier transform infrared spectrometer is a Michelson interferometer with a movable mirror. By scanning the movable mirror over some distance, an interference pattern is produced that encodes the spectrum of the source (in fact, it turns out to be its Fourier transform). Fourier transform spectrometers have a multiplex advantage over dispersive spectral detection techniques for signal, but a multiplex disadvantage for noise. In its simplest form, a Fourier transform spectrometer consists of two mirrors located at a right angle to each other and oriented perpendicularly, with a beamsplitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors. Radiation incident on the beamsplitter from one of the two "ports" is then divided into two parts, each of which propagates down one of the two arms and is reflected off one of the mirrors. The two beams are then recombined and transmitted out the other port. When the position of one mirror is continuously varied along the axis of the corresponding arm, an interference pattern is swept out as the two phase-shifted beams interfere with each other.
Usually the scientists are interested in transmission or absorption type experiments, where the total light intensity $I_t$ transmitted after the light passes through a sample is measured as a function of wavelength and ratioed versus the light intensity $I_{r0}$ recorded when no sample is present. What the Michelson interferometer produces, however, is the interferogram: a digital plot of light intensity versus mirror position (in cm). Only when a mathematical function known as the digital Fourier transform (FT) is applied to the data does one obtain a single beam spectrum of intensity $I_t$ versus wavenumber (in cm$^{-1}$).

For a transmission measurement there are actually two experiments that are carried out sequentially: First an interferogram measurement is made with no sample present; this is Fourier-transformed to yield the single beam reference (SBR) or $I_0$ spectrum. In the next measurement, the sample is placed in the beam, and the mirror is scanned to produce a second interferogram with a different pattern, usually of smaller amplitude due to some of the light being absorbed or scattered by the sample. This second spectrum is then Fourier-transformed to yield the single beam sample (SBS) or $I_t$ spectrum. Having obtained these two spectra, they can be manipulated in the usual ways to yield either a transmittance [$I_t / I_0$] or absorbance [$-\log (I_t / I_0)$] spectrum (Fig.2.17) [79, 80].

### 2.2.5.3 Fundamentals of Fourier transform infrared absorption

Absorption of FTIR is restricted to compounds with small energy differences in the possible
vibrational and rotational states. For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (electromagnetic radiation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. The bonds that hold a molecule together and the masses of the constituents are so related that the molecule exerts radiation of a frequency, corresponding to one of its normal vibrating frequencies, for the incident beam. Therefore, the absorption bands in an infrared spectrum are at frequencies corresponding to the frequencies of vibration of the molecule concerned [74].

It is important to reflect on the distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (Eqn.2.9):

\[ E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{translational}} \]  

(2.9)

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The electronic component is linked to the energy transitions of electrons as they are distributed throughout the molecule, either localized within specific bonds, or delocalized over structures, such as an aromatic ring. Every material is permeable to electromagnetic radiation over a wide range, while at certain wavelengths it can be absorbant. So in order for the energy to be absorbed, the frequency of the incident light must corresponds exactly to the energy difference between the two energy states concerned (Eqn.2.10):

\[ E_1 - E_2 = h \nu \]  

(2.10)

The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study [81].

Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinate axes (x, y, z). A polyatomic molecule of n atoms has 3n total degrees of freedom. However, 3 degrees of freedom are required to describe translation, the motion
of the entire molecule through space. Additionally, 3 degrees of freedom correspond to rotation of the entire molecule. Therefore, the remaining $3n - 6$ degrees of freedom are true, fundamental vibrations for nonlinear molecules. Linear molecules possess $3n - 5$ fundamental vibrational modes because only 2 degrees of freedom are sufficient to describe rotation. Among the $3n - 6$ or $3n - 5$ fundamental vibrations (also known as normal modes of vibration), those that produce a net change in the dipole moment may result in an IR activity.

2.2.5.4 Summary of absorptions of bonds in organic molecules

![Fig.2.18 Infrared spectroscopy correlation table.](image)

2.2.5.5 Infrared activity

Not all possible vibrations within a molecule will result in an absorption band in the infrared region. To be infrared active the vibration must result in a change of dipole moment during the vibration. This means that for homonuclear diatomic molecules such as Hydrogen ($H_2$), $N_2$ and Oxygen ($O_2$) no infrared absorption is observed, as these molecules have zero dipole moment and stretching of the bonds will not produce one. For heteronuclear diatomic molecules such Carbon Monoxide (CO) and Hydrogen Chloride (HCl), which do possess a
permanent dipole moment, infrared activity occurs because stretching of this bond leads to a
change in dipole moment (since Dipole Moment = Charge × Distance). It is important to
remember that it is not necessary for a compound to have a permanent dipole moment to be
infrared active. In the case of Carbon Dioxide (CO₂) the molecule is linear and
centrosymmetric and therefore, does not have a permanent dipole moment. This means that
the symmetric stretch will not be infrared active. However, in the case of the asymmetric
stretch a dipole moment will be periodically produced and destroyed resulting in a changing
dipole moment and therefore infrared active.

Assignments for stretching vibrations can be approximated by the application of Hook’s
law. In the application of the law, 2 atoms and their connecting bond are treated as a simple
harmonic oscillator composed of 2 masses joined by a spring. The following equation,
derived from Hook’s law, states that, the vibrational frequency

\[ \nu = \frac{1}{2 \pi c} \left( \frac{F}{m_x m_y} \right)^{\frac{1}{2}} \]  

(2.11)

Where \( c = \) velocity of light (cm/sec), \( F = \) Force constant of bond (dynes/cm), \( m_x \) and \( m_y \) =

mass (g) of atom x and atom y, respectively [73].

i. Factors influencing number of absorption bands

* Overtone bands: Absorption at frequencies representing the fundamental frequencies at
the multiples of the fundamentals.

* Combination bands: Two fundamental vibrations interact and are influenced by radiation
at the combined frequency.

* Vibrational-Rotational bands: The single vibrational band is accompanied by a series of
subsidiary bands both at lower and higher frequencies. Gas spectra are commonly
characterized by very complex vibration-rotation systems.

* Harmonic coupling bands: Interaction from adjacent groups of nearly identical oscillation
frequencies produces a series of bands quite apart from those normally expected. This
phenomenon is relatively uncommon.

ii. Factors limiting the number of absorption bands

The total number of observed absorption bands is generally different from the total number
of fundamental vibrations. It is reduced because some modes are not IR active and a single
frequency can cause more than one mode of motion to occur. Conversely, additional bands
are generated by the appearance of overtones (integral multiples of the fundamental
absorption frequencies), combinations of fundamental frequencies, differences of fundamental frequencies, coupling interactions of two fundamental absorption frequencies, and coupling interactions between fundamental vibrations and overtones or combination bands (Fermi resonance). The intensities of overtone, combination, and different bands are less than those of the fundamental bands. The combination and blending of all the factors thus create a unique IR spectrum for each compound. Infrared radiation is absorbed and the associated energy is converted into these types of motions. The absorption involves discrete, quantized energy levels. However, the individual vibrational motion is usually accompanied by other rotational motions.

* No change in dipole moment due to symmetry.

* Degeneracy: Vibrational frequencies located too closely.

* Weak absorptions.

### 2.2.6 Ultraviolet Visible Optical Absorption Spectroscopic Analysis

Most materials absorb some light and the degree to which they absorb light is a function of the wavelength of the light. Because optical absorption in the visible and near-UV portions of the spectrum is generally the result of absorption of light by electrons in atoms, ions or molecules, the absorption characteristics can yield a considerable amount of information regarding their electronic structure. The visible region of the spectrum comprises photon energies of 36 to 72 Kcal/mole and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. In the most important region where most investigations are carried out, namely between 200 and 600 nm, there are electronic transitions of double bonds.

#### 2.2.6.1 Electronic transitions

The absorption of UV or visible radiation corresponds to the excitation of outer electrons. There are three types of electronic transition which can be considered;

- Transitions involving π, σ, and n electrons
- Transitions involving charge-transfer electrons
- Transitions involving d and f electrons

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be
considered as being packed on top of each electronic level [81]. The energy absorbed is
dependent on energy difference between the ground state and excited state; the smaller the
difference in energy, the longer the wavelength of absorption. The excess energy in the
excited state may result in dissociation or ionization of the molecule, or it may be reemitted
as heat or light.

![Energy Levels](image)

**Fig. 2.20 Vibrational and rotational energy levels of absorbing materials.**

The principle characteristics of an absorption band are its position and intensity. The
position of absorption corresponds to the wavelength of radiation whose energy is equal to
that required for an electronic transition. The intensity of absorption is largely dependent on
two factors: the probability of interaction between the radiation energy and the electronic
system and the difference between the ground and excited state [73].

### 2.2.6.2 Absorbing species containing $\pi$, $\sigma$, and $n$ electrons

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain
functional groups (chromophores) that contain valence electrons of low excitation energy.
The spectrum of a molecule containing these chromophores is complex. This is because the
superposition of rotational and vibrational transitions on the electronic transitions gives a
combination of overlapping lines. This appears as a continuous absorption band. Possible
electronic transitions of $\pi$, $\sigma$, and $n$ electrons are;

- **$\sigma \rightarrow \sigma^*$ Transitions**
  
  An electron in a bonding $\sigma$ orbital is excited to the corresponding antibonding orbital. The
  energy required is large. For example, methane (which has only C-H bonds and can only
  undergo $\sigma \rightarrow \sigma^*$ transitions) shows an absorbance maximum at 125 nm. Absorption maxima
due to $\sigma \rightarrow \sigma^*$ transitions are not seen in typical UV-vis. spectra (200 - 700 nm).
**n→σ** Transitions
Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of **n→σ** transitions. These transitions usually need less energy than **σ→σ** transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with **n→σ** peaks in the UV region is small.

**n→π** and **π→π** Transitions
Most absorption spectroscopy of organic compounds is based on transitions of **n** or **π** electrons to the **π** excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm).

**2.2.6.3 Direct and indirect optical transitions**
Most materials absorb some light and the degree to which they absorb light is a function of the wavelength of the light. Because optical absorption in the visible and near-UV portions of the spectrum is generally the result of absorption of light by electrons in atoms, ions or molecules, the absorption characteristics can yield a considerable amount of information regarding their electronic structure.

The Beer Lambert law states that, “When a beam of monochromatic radiation passes through a homogeneous absorbing medium; the rate of decrease in intensity of electromagnetic radiation in UV-vis region with thickness of the absorbing medium is proportional to the intensity of the incident radiation”. This gives the equation,

\[ I_r = I_0 e^{-\alpha d} \]  

(2.12)
\[ \log_e \left( \frac{I_0}{I_r} \right) = ad \] (2.13)

Where \( I_0 \) is the intensity of the incident radiation, \( I_r \) is the intensity of the transmitted radiation, \( d \) is the path length of the absorbing species and \( \alpha \) is the absorption co-efficient.

The absorption coefficient, \( \alpha \) can be calculated using the following eqn.

\[ \alpha = 2.303 \frac{A}{d} \] (2.14)

Where, \( \alpha \) is the absorption coefficient, \( A = \log_e \left( \frac{I_0}{I_r} \right) \) is the absorbance, and \( d \) is the thickness of the film.

The mechanism of photoconduction in semiconductors is schematically illustrated in Fig. 2.22, which plots the \( E-k_v \) diagrams for a direct band gap material (left) and an indirect gap material (right), where \( E \) and \( k_v \) are respectively the kinetic energy and wave vector (or "momentum vector") of the electron or hole \( (E = \frac{1}{2} \hbar^2 k_v^2 / 2m^* \) where \( \hbar \equiv h / 2\pi \) is the reduced Planck constant and \( m^* \) is the electron or hole effective mass). The direct and indirect gap materials are distinguished by their relative positions of the conduction band minimum and the valence band maximum in the Brillouin zone (the volume of \( k_v \) space containing all the values of \( k_v \) up to \( \pi/a \) where \( a \) is the unit lattice cell dimension). In a direct gap material, both the conduction band minimum and the valence band maximum occur at the zone center where \( k_v = 0 \). In an indirect gap material, however, the conduction band minimum does not occur at \( k_v = 0 \), but rather at some other values of \( k_v \) which is usually at the zone edge or close to it [82].

Upon absorption of an UV or visible photon with an energy \( h\omega_{exc} \) exceeding the band gap \( E_g \) (the gap in energy between the valence band and the conduction band) of the material, an electron-hole pair is created and the electron (hole) is excited to states high up in the conduction (valence) band (Fig.2.22).

During a photon absorption process in semiconductors, both energy and momentum must conserve. In a direct band gap material, the conduction band minimum and the valence band maximum have the same \( k_v \) values (i.e., \( h\vec{k}_{vi} = h\vec{k}_{vf} \) where \( \vec{k}_{vi} \) and \( \vec{k}_{vf} \) are respectively the wave vectors of the initial and final electron states; this implies that the electron wave vector should not change significantly during a photon absorption process), conservation of momentum is guaranteed for the photoexcitation of the electron which only involves a UV or visible photon: \( h\vec{k}_{vi} + h\vec{k}_{v\text{phot}} \approx h\vec{k}_{vf} = h\vec{k}_{vf} \) since \( \vec{k}_{v\text{phot}} \), the wave vector of the absorbed photon (which is in the order of \( 2\pi / \lambda \sim 10^5 \text{ cm}^{-1} \)), is negligible compared to the electron wave vector (which is related to the size of the Brillouin zone \( \pi/a \sim 10^8 \text{ cm}^{-1} \), where the unit cell dimension \( a \) is in the order of a few angstroms). This implies that in a
direct band gap material, the electron wave vector does not change significantly during a photon absorption process. Therefore, the photon absorption processes can be represented by vertical arrows in the $E$-$k_v$ diagrams (Fig.2.22). In contrast, for an indirect band gap material of which the conduction band minimum and the valence band maximum have different $k_v$ values (Fig.2.22), conservation of momentum implies that the photon absorption process must be assisted by either absorbing or emitting a phonon (a quantum of lattice vibration), because the electron wave vector must change significantly in jumping from the valence band in state $(E_i, k_vi)$ to a state $(E_f, k_vf)$ in the conduction band, and the absorption of a photon alone can not provide the required momentum change since $|k_{\text{photon}}| \ll |k_{vi} - k_{vf}|$. The excited electron and hole will not remain in their initial excited states for very long; instead, they will relax very rapidly ($\sim 10^{-13}$ s) to the lowest energy states within their respective bands by emitting phonons. When the electron (hole) finally arrives at the bottom
(top) of the conduction (valence) band, the electron-hole pair can recombine radiatively with the emission of a photon (luminescence), or nonradiatively by transferring the electron's energy to impurities or defects in the material or dangling bonds at the surface.

Just like the photon absorption process discussed above, the electron-hole recombination in a direct band gap material does not involve any phonons since there is no need for momentum change for the electron. In contrast, in an indirect gap material, the excited electron located in the conduction band needs to undergo a change in momentum state before it can recombine with a hole in the valence band; conservation of momentum demands that the electron-hole recombination must be accompanied by the emission of a phonon, since it is not possible to make this recombination by the emission of a photon alone. Compared to the photon absorption process in an indirect gap material for which conservation of momentum can be fulfilled by either absorption or emission of a phonon, in the electron-hole recombination process phonon absorption becomes negligible, whereas phonon emission becomes the dominant momentum conservation mediator because (1) the number of phonons available for absorption is small and is rapidly decreasing at lower temperatures, whereas the emission of phonons by electrons which are already at a high-energy state is very probable; and (2) an optical transition assisted by phonon emission occurs at a lower photon energy $E_g - h\nu_{\text{phon}}$ than the gap energy, whereas phonon absorption results in a higher photon energy of at least $E_g + h\nu_{\text{phon}}$, which can be more readily re-absorbed by the semiconductor nanoparticle. But it can be noted that the energy of a phonon ($h\nu_{\text{phon}}$) is just in the order of $\sim 0.01$ eV, much smaller than the energy of the electron-hole recombination luminescence photon [83].

For higher photon energies the simplified general equation is

$$a h\nu = B(h\nu - E_g)^n$$

where, $h\nu$ is the energy of absorbed light, $n$ is the parameter connected with distribution of the density of states and $B$, a constant or Tauc parameter and here $n = 1/2$ for direct and $n = 2$ for indirect transitions [84]. The absorption coefficient, $a$, at various wavelengths can be calculated using the Eqn (2.15). The plot of $(a h\nu)^{1/2}$ as a function of $h\nu$ is for indirect transition and the plot of $(a h\nu)^2$ as a function of $h\nu$ is for direct transition. The optical transition energy gap ($E_g$) values can be obtained by extrapolating the linear portion of the plots to the intercept of the photon energy axis.

The band gap in polymer films is not well defined since the film consists of several chain segments that correspond to a distribution of band gaps. This is due to variations in chain
lengths of the polymers or defects related to morphological disorder, chemical defects, interaction with the solution or carrying surface, etc. The band gap value is therefore an average of all polymer chains that together are building up the solid film or solution. The energy gap in a conjugated polymer typically ranges from 1 to 4 eV [85].

2.2.6.4 Charge - Transfer absorption
Many inorganic species show charge-transfer absorption and are called charge-transfer complexes. For a complex to demonstrate charge-transfer behaviour, one of its components must have electron donating properties and another component must be able to accept electrons. Absorption of radiation then involves the transfer of an electron from the donor to an orbital associated with the acceptor.

2.2.6.5 Urbach tail analysis, steepness parameter and extinction co-efficient
In 1953 Urbach proposed an empirical rule for the optical absorption coefficient ($\alpha$) associated with the electronic transition from the valance to conduction band tail in disordered solids. This rule states that $\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$ where $\alpha_0$ is a constant and $E_u$ is the Urbach energy. Subsequent experimental analysis of Urbach tail in a variety of disordered semiconductors and glasses exhibiting this Urbach exponential spectral behavior strongly suggested that the Urbach absorption edge is nearly a universal property of the disordered solids and that the underlying physics is both simple and general and can be applied to polymeric materials also. In contrast theoretical efforts by various researchers focused on a variety of fundamentally different physical origins of the Urbach edge, suggested that the underlying physics changes completely for tail states near the band edge where the kinetic energy of localization plays a dominant role in determination of the scale of the most probable potential fluctuations. The other models for the explanation of the Urbach tail are the density of states of the electron band tail at the absorption edge. The universally observed Urbach tail and the dependence of different parameters are not able to determine from these models since the applications of these are specific. The disorder giving rise to the exponential band tails is produced by lattice vibration, impurities and other deviations from the perfect periodicity of the lattice. The effect of thermal and structural disorder on the electronic state of the hydrogenated amorphous silicon is investigated by Cody et al. It is observed that the thermal and structural disorder are additive and suggest that the disorder is a fundamental factor in the $E_g$. In the case of crystalline semiconductors the width of the exponential tail is a direct measurement of the temperature independent component of
Urbach edge. The presence of impurity levels or the dopants contributes to the optical absorption because they create charged defect and defect levels. The density of states ($\rho(E)$) of a particle, for example, has an electron interacting with charged centers which are randomly located in a highly disordered material, is of utmost importance.

When the disorder is large, the edges of the allowed energy bands develop band tails reaching into the energy gaps. The form of these band tails can be expressed as

$$\rho(E) \propto \exp \left( -\frac{E^n}{E_0} \right)$$  \hspace{1cm} (2.16)

$n=1$ for the Urbach tail where $E$ is measured away from the band edge $E_0$. Since the absorption coefficient is proportional to $\rho(E)$, with $n=1$. Here $E_0=\hbar/\omega_0$ plays the role of effective band edge energy. The review of the experimental data from the literature showed that the absorption coefficient varies as a few orders of magnitude within a small energy region near the absorption edge [86]. Thus, The spectral dependence of $\alpha$ can be studied at photon energies less than the energy gap of the films, i.e. in the region of the so called Urbach spectral tail, which characterizes the slope of the exponential edge and is expressed as [87]

$$\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)$$  \hspace{1cm} (2.17)

where $\alpha_0$ is a constant, $h\nu$ is the photon energy and $E_u$ is the Urbach energy.

The Urbach energy characterizes the slope of the exponential edge region and the inverse of the slope gives the width of the localized states associated with amorphous state in the band gap. $E_u$ value that determines the steepness of the Urbach tail depends on the structural disorder of sample. The Urbach energy $E_u$ is given as Eqn. (2.18).

$$E_u = k_B T / \sigma_s$$  \hspace{1cm} (2.18)
where $\sigma_s$ is steepness parameter which characterizes the steepness or width of the straight line in the vicinity of the band edge or the broadening of the optical absorption edge due to electron-phonon or exciton-phonon interactions, $k_B$ is Boltzmann constant and $T$ is the absolute temperature. Urbach energy is calculated by fitting an exponential function to the slope of the linear portion of $\ln \alpha$ vs. $h\nu$ plot.

The extinction coefficient, $K$, indicates the amount of absorption loss when the electromagnetic wave propagates through the material. This coefficient, $K$ is an optical property of the semiconductor material and is related to the index of refraction $n$, which merely determines how much light is absorbed by the material. $K > 0$ means absorption, while $K=0$ means the light travels straight through the material. The absorption and extinction coefficients are related by the following equation:

$$\alpha = \frac{4\pi fK}{c}$$

(2.19)

Where, $f$ is the frequency of the monochromatic light (related to the wavelength by $\lambda=\nu/f$, where $\nu$ is the velocity of the light wave), $c$ is the speed of light.

### 2.2.7 DC Electrical Conduction Mechanisms

Electrical properties of insulating polymers are there responses when an electric field is applied to them. The subject of electrical properties of polymers covers an extremely diverse range of molecular phenomena. In contrast to metals, in which the electrical field response is one of electronic conduction, polymers may respond in a more varied manner, and a whole set of delicate electrical effects may be observed. No known polymer is completely free of conduction processes, however small the quantity of charge carriers it may possess. Low level conduction in insulating polymers can take a variety of forms. Conduction may very often be contributed by impurities that provide a small concentration of charge carriers in the form of electrons or ions. At high fields, the electrodes may inject new carriers (holes and electrons) into polymers. At very high fields, these and other processes will lead to complete breakdown of polymers as insulating materials. The imposition of an electrical field upon a polymer will cause a redistribution of any charges in the polymer, provided they are mobile enough to respond in the time scale in the applied field. If some of the mobile charges are able to diffuse throughout the specimen and charge migration through the electrode sample interface is possible, then the charges will support a DC conductance. It should be mentioned that the vacuum-deposited thin film insulators can
contain a large density of both impurity and trapping centers. A well judged study of electrical conduction in vacuum deposited thin films cannot be accomplished without consideration of these possibilities [88].

- **Metal-Insulator contacts**
  In order to measure the conductivity of an insulator, it is necessary to connect electrodes to its surfaces in order to facilitate injection of electrodes into and their withdrawal from the bulk of the insulator. The action of the insulator is to erect between the electrodes a potential barrier, extending from the electrode Fermi level to the bottom of the insulator conduction band. This barrier impedes the flow of electrons from one electrode to the other, which would normally flow virtually unimpeded if the insulator were not there (i.e. metal-metal contact). The shape of the potential barrier just within the surface of the insulator depends on whether or not the insulator intrinsic or extrinsic and on the relative magnitudes of the work functions of the metal and insulator, among other things.

  At reasonable applied fields there will normally be a sufficient supply of carriers available to enter the insulator from the cathode (negatively biased electrode) to replenish the carrier drawn out of the bulk of the insulator. Under these conditions the $I-V$ characteristics of the sample will be determined by the bulk properties of the insulator and this process is referred to as bulk-limited. At high fields, or if the contact is blocking, the current capable of being supplied by the cathode to the insulator will be less than that capable of being carried in the bulk of the insulator. Under these conditions the $I-V$ characteristics of the sample will be controlled primarily by condition existing at the cathode-insulator interface, this conduction process is referred to as being emission limited or contact limited.

- **Power law**
  A power law can express the variation of current density with voltage in a material generally:

  $$J \propto V^n$$

  (2.20)

  where, $n$ is a power factor. When $n$ is unity, the conduction is Ohmic. If the value of $n$ is less or more than unity, then the conduction process is other than Ohmic.

  Many scientists have investigated three worth-mentioning electrical conduction mechanisms which are operative in the thin films of various organic compounds [4, 16, 47-57]:

  - The injection of carriers from the electrode by means of thermal or field assisted emission usually referred to as Schottky emission.
The other process in which carriers are produced by the dissociation of donor-acceptor centers in the bulk of the material, is called PF generation.

If the generation process is slower than transport by the carriers through the material, the conduction is controlled by generation, specifically by either the Schottky or PF mechanism. Conversely, when the transport is slower than generation, it constitutes the rate-determining step, and the conduction is described by the theory of space-charge-limited current (SCLC). The phenomenon is, if a charge is injected at the electrode-polymer interface, a large excess carrier density at the injecting electrode will exist and a SCLC will flow [4].

A brief explanation of these conduction mechanisms is stated below.

- **Electrode-limited process**

The electron current flowing between two metal electrodes separated by an insulator is given by

\[
J = 4\pi \frac{e_m}{h^3} \int_0^\infty dE (f_c(E) - f_a(E)) \int_0^E \rho(E_x) dE_x
\]

(2.21)

Where \(e\) is the electronic charge; \(h\) is Planck’s constant;

\[
f_c = \left\{1 + \exp\left(\frac{E - E_{fc}}{k_B T}\right)\right\}^{-1}
\]

and

\[
f_a = \left\{1 + \exp\left(\frac{E + eV - E_{fa}}{k_B T}\right)\right\}^{-1}
\]

are respectively the electron distributions in the cathode and anode electrodes; \(E_{fc}\) is the Fermi energy of the cathode; \(V\) is the voltage difference between the cathode and anode; \(E\) and \(E_x\) are respectively the energy and ‘x-directed’ energy of the electron; and \(P(E_{ci})\) is the electron transmission probability through the insulator.

- **Thermionic emission**

When the potential barrier is too thick at sufficiently high temperature, the current flowing through the insulator is limited principally by the rate at which electrons are thermally excited over the interfacial potential barrier into the insulator conduction band. Thus, in order to determine the current flowing in the system, we set the lower limit in the integral over \(dE_x\) in Eqn 2.21 to be equal to the interfacial barrier height \(\phi\) and the transmission function \(T(E_{ci})\) to unity. Eqn 2.21 then integrates to

\[
J = \frac{4\pi m e k_B^2 T^2}{h^3} \exp\left(-\frac{\phi}{k_B T}\right) \equiv A \phi T^2 \exp\left(\frac{\phi}{k_B T}\right)
\]

(2.22)

which is the Richardson (saturated) thermionic emission equation if \(\phi\) is independent of the voltage bias [88].
2.2.7.1 Schottky mechanism

Charge injected from a metal to an insulator or semiconductor at medium fields may take place by field-assisted thermionic emission, a process known as Richardson-Schottky effect or simply Schottky emission. This is a procedure of image force induced lowering potential energy for charge carrier emission when an electric field is applied. The potential step changes smoothly at the metal insulator interface as a result of the image force. This happens when the metal surface become polarized (positively charged) by an escaping electron, which in turn exerts an attractive force $F_{im} = -\frac{e^2}{16\pi\varepsilon_0\varepsilon'x^2}$ on the electron. The potential energy of the electron due to the image force is thus

$$\phi_{im} = -\frac{e^2}{16\pi\varepsilon_0\varepsilon'x}$$

(2.23)

where $x$ is the distance of electron from the electrode surface.

The potential step at a neutral barrier with attendant image potential as a function of the distance $x$ from the interface is given by,

$$\phi(x) = \phi_0 + \phi_{im} = \phi_0 - \frac{e^2}{16\pi\varepsilon_0\varepsilon'x}$$

(2.24)

where $\phi_0$ = Coulombic barrier height of the electrode-polymer interface in Schottky conduction. The barrier potential $\phi(x)$ in the presence of image forces is illustrated by the line AB in Fig.2.23. Schottky assumed that the image force holds only for $x$ greater than some critical distance $x_0$. For $x < x_0$, he assumes a constant image force, i.e. the potential energy is a linear function of $x$, and such that it matches the bottom of the electrode conduction band at the surface.
When an electric field exists at a metal-insulator interface, it interacts with the image force and lowers the potential barrier. The line CD represents the potential due to a uniform applied field. The dotted line represents the potential $\Delta \phi$, when the potential due to a uniform electric field is added to the barrier potential $\phi(x)$ and thus it is lower than that of without the electric field. Under the influence of the field the potential energy of the barrier with respect to Fermi level of the electrode can be given by

$$\phi(x) = \phi_0 - \frac{e^2}{16 \pi \varepsilon' \varepsilon_0 x} - eFx$$  \hspace{1cm} (2.25)

This equation has a maximum at $x_m = \left( \frac{e}{16 \pi \varepsilon' \varepsilon_0 F} \right)^{1/2}$

Therefore, the change $\Delta \phi_s = \phi_0 - \phi(x_m)$ in the barrier height due to the interaction of the applied field with the image potential can be given by

$$\Delta \phi_s = \left( \frac{e^3}{4 \pi \varepsilon' \varepsilon_0} \right)^{1/2} F_s^{1/2} = \beta_s F_s^{1/2}$$ \hspace{1cm} (2.26)

Substituting $\phi(x_m) = \phi_0 - \Delta \phi_s$ for $\phi$ in Eqn 2.22 we obtain

$$J = A_R T^2 \exp\left( -\frac{\phi_0 - \Delta \phi_s}{k_B T} \right)$$ \hspace{1cm} (2.27)

$$J = A_R T^2 \exp\left( \frac{\beta_s F_s^{1/2} - \phi_0}{k_B T} \right)$$ \hspace{1cm} (2.28)

which is the Richardson-Schottky law.

where, $A_R = 1.20173 \times 10^6 \text{ Am}^{-2}\text{K}^{-2}$ is the effective Richardson constant, $F_s = \text{static electric field}$ and is equal to $V/d$, $V = \text{applied voltage}$, $d = \text{film thickness}$, $T = \text{temperature in Kelvin}$, $k_B = \text{Boltzmann constant}$ and $\beta_s$ is the Schottky coefficient which is given by,

$$\beta_s = \left( \frac{e^3}{4 \pi \varepsilon' \varepsilon_0} \right)^{1/2}$$ \hspace{1cm} (2.29)

where, $e = \text{elementary charge of the electron}$ and $\varepsilon'$ is the high frequency dielectric constant of the material.

The electrode limited Richardson-Schottky effect in insulators appears to have been first observed by Emptage and Tantraporn, who reported a log $I$ vs. $F_s^{1/2}$ relationship in their samples. It was suggested that the plot should have to be linear in nature for Schottky type conduction mechanism [88, 89].
2.2.7.2 Schottky barrier height

One of the most interesting properties of any metal-semiconductor (MS) interface is its Schottky barrier height (SBH). The SBH is the rectifying barrier for electrical conduction across the MS junction and, therefore, is of vital importance to the successful operation of any semiconductor device. The magnitude of the SBH reflects the mismatch in the energy position of the majority carrier band edge of the semiconductor and the metal Fermi level across the MS interface. At a metal/n-type semiconductor interface, the SBH is the difference between the conduction band minimum and the Fermi level. And for a p-type interface, the SBH is the difference between the valence band maximum of the semiconductor and the metal Fermi level. The most common symbol for the SBH is $\Phi_B$.

The first-order theory of the formation of a Schottky barrier (SB) is the view attributed to W. Schottky himself originally and also to Sir Mott. The Schottky-Mott theory proposes that the SBH depends sensitively on the work function of the metal. However, this prediction has received little support from experiment. The SBHs measured in actual experiments often showed some dependence on the preparation of the MS interface, which indicates that the SBH depends more than just the work function of the metal. Despite some scatters in the experimental data, by and large, metals with larger work functions have been found to have systematically higher SBHs than those with lower work functions. But the
actual dependence observed is much weaker than that predicted by the Schottky-Mott theory. A term, "Fermi level (FL) pinning", has often been used to describe the insensitivity of the experimental SBH to the metal work function.

2.2.7.3 Poole-Frenkel mechanism

The PF conduction mechanism is a field assisted thermal ionization process and is the bulk analogue of the Schottky effect at an interfacial barrier. This effect is lowering of a Coulombic potential barrier when it interacts with an electric field, as shown in Fig 2.23.

The PF lowering of a Coulombic barrier $\Delta \phi_{PF}$ in a uniform electric field is twice that due to the Schottky effect at a neutral barrier, because the potential energy of an electron in a Coulombic field $-\frac{e^2}{4\pi\varepsilon_0\varepsilon x}$ is four times that due to image force effects in Schottky mechanism; i.e.

$$\Delta \phi_{PF} = 2\Delta \phi_s = 2\left(\frac{e^3}{4\pi\varepsilon_0\varepsilon}\right)^{1/2} F_s^{1/2} \equiv \beta_{PF} F_s^{1/2}$$

where, $\beta_{PF}$ is PF coefficient.

From this it can be concluded that,

$$\beta_{PF} = 2\left(\frac{e^3}{4\pi\varepsilon_0\varepsilon}\right)^{1/2} = 2\beta_s$$

i.e. $2\beta_s = \beta_{PF}$

In the bulk limited PF mechanism, the thermal emission of trapped carriers from the bulk material gives rise to conductivity

$$J = \sigma_0 F_s \exp\left(\frac{\beta_{PF} F_s^{1/2} \phi_c}{k_B T}\right)$$

Fig.2.26 Poole-Frenkel effect at a donor center.
where, $\phi_c$ is the ionization potential of the PF centers.

Consequently, a general expression of the form

$$ J = J_0 \exp \left( \frac{\beta F_{s}^{1/2} - \phi}{k_B T} \right) $$

holds equally well for both Schottky and PF mechanisms. Where, $J$ is the current density at a biased voltage.

By taking natural logarithms of Eqn. 2.34 we can write,

$$ \beta_{exp} = s k_B T d^{1/2} $$

where, $\beta_{exp}$ denotes the value of $\beta$ obtained experimentally and $s = \frac{\Delta \ln J}{\Delta V^{1/2}}$ is the slope of graph plotted between $\ln J$ and $V^{1/2}$.

### 2.2.7.4 Space charge limited conduction mechanism

When an Ohmic contact is made to the insulator, the space charge injected into the conduction band of the insulator is capable of carrying current and when the transport is slower than generation, it constitutes the rate-determining step, and the conduction is described by the theory of SCLC [88]. When a voltage bias is applied to the metal electrodes, this results an addition of positive charge to the anode and negative charge to the cathode. If now the voltage bias increases, the net positive charge on the anode increases and that on the cathode decreases. Assuming that the anode region extends throughout the insulator and neglecting the diffusion effect the current can be interpreted by the Mott and

![Fig.2.27 Energy diagram for different regions under space charge limited conduction mechanism.](image)
Gurney relation [89]

\[ J = \frac{9 \mu \varepsilon' \varepsilon_0 V^2}{8d^3} \]  \hspace{1cm} (2.36)

Where, \( \mu \) is the mobility of charge carriers, \( \varepsilon' \) is dielectric constant, \( \varepsilon_0 \) is the permittivity of free space, \( V \) is the applied voltage and \( d \) is the thickness. If the insulator contains \( N_t \) shallow traps positioned an energy \( E_t \) below the conduction band then the free component of the space charge

\[ \rho_f = eN_c \exp \left( - \frac{E_F}{kT} \right) \]  \hspace{1cm} (2.37)

and trapped component of space charge

\[ \rho_t = eN_t \exp \left( - \frac{E_t}{kT} \right) \]  \hspace{1cm} (2.38)

thus trapping factor, \( \theta \) is defined as

\[ \theta = \frac{\rho_f}{\rho_t} = \frac{N_c}{N_t} \exp \left( - \frac{E_F}{kT} \right) \]  \hspace{1cm} (2.39)

where \( N_c \) is the effective density of states in the conduction band, and \( N_t \) the density of trapping levels situated at an energy \( E_s \) below the conduction band edge.

The SCLC current density with traps is defined by

\[ J = \frac{9 \mu \varepsilon' \varepsilon_0 V^2}{8d^3} \theta \]  \hspace{1cm} (2.40)

For a shallow trap SCLC and trap-free SCLC, \( \theta = 1 \). According to Eqn. 2.40, \( J \) varies as \( d^{-1} \) in the Ohmic region and as \( d^{-3} \) in the SCLC region for the trap-filled SCLC part. For a fixed \( V \), the dependence of \( \ln J \) on \( \ln d \) should be linear with slope \( l \geq -3 \).

Lampert calculated the voltage at which the transition from the Ohmic to shallow trap SCLC region \( (V_{tr}) \) occurs is given by

\[ V_{tr} = \frac{8}{9} n_0 \frac{ed^2}{\varepsilon} \]  \hspace{1cm} (2.41)

Where, volume generated free carrier density, \( n_0 \) is independent of both \( \mu \) and \( J \) [4].

According to Fig.2.27 it was found that the second linear region would extend up to a certain voltage, called as the crossover voltage, and beyond which the current would vary with the voltage as a power law:
\[ J \propto V^2 \]  
\[ \text{(2.42)} \]

Which would continue until the current is close to the saturation current, i.e. the maximum current that the electrode could supply. However in real samples which contain several trap sites to capture the electrons that had been injected inside the sample. There are two types of traps; the ones above the Fermi level are the shallow traps, and the others below the Fermi level being the deep traps. During trapping both shallow and deep traps would get filled. The voltage at which all the traps would get completely filled is called the trap filled limit (TFL). Beyond \( V_{TFL} \) all the excess charges would be injected into the conduction band and the current would approach the trap free square law as described in Eqn. 2.42 [88, 89].

Fig.2.28 Space charge limited conduction characteristic for an insulator containing shallow traps.

2.2.7.5 Thermally activated conduction processes

Electronic conduction in organic, molecular compounds differs in several important ways from the more familiar kind in metals and semiconductors. An important feature of the band system is that electrons are delocalized and spread over the lattice. Some delocalization are naturally expected when an atomic orbital of any atom overlaps appreciably with those of more than one of its neighbors, but delocalization reaches an extreme form in the case of a regular 3 dimensional lattice. The band theory assumes that the electrons are delocalized and can extend over the lattice. When electronic conduction is considered in polymers, band theory is not totally suitable because the atoms are covalently bonded to one another,
forming polymeric chains that experience weak intermolecular interactions. But macroscopic conduction will require electron movement, not only along the chain but also from one chain to another.

The electrical resistance of plasma polymerized thin films show high values and hence the transport properties in a metal-polymer- metal (M-P-M) structure, a carrier on one side can move to the other side either by tunneling through the barrier or by moving over the barrier via an activated state. The second process is called hopping. Though polymer are amorphous materials, short range order prevails in most of these materials, and the theory that is used to explain electronic band structure in amorphous materials can be extended to the case of polymers too. If the spatial fluctuations of inter atomic distances are large, the correspondingly large and random fluctuation in the height or depth of the potential wells may lead to the localization of states below a certain critical and well defined energy. When the carrier mobility is low and the mean free path is comparable with inter atomic distance, the conduction can be expected to take place by a hopping process in the localized states. In hopping mechanism, only those carriers with an energy $k_B T$ below the fermi level have a significant probability of hopping. The expressions or conductivity in this case is given by

$$\sigma_{dc} = n E_F \alpha_a e^2 \alpha^2 \hbar \nu \exp\left(-\Delta E/k_B T\right)$$

(2.43)

where $n E_F$ is the density of states at the Fermi level, $\alpha_a$ is a parameter depending on the exponent of overlap of localized states, $e$ is the electronic charge, $a$ is the number of electrons per unit volume, $\hbar \nu$ is the phonon frequency and $\Delta E$ is the activation energy for hopping. The conductivity thus shows exponential temperature dependence. Mott has shown that for strongly localized states, the conductivity at low temperature must follow a relationship,

$$\sigma_{dc} = e \exp\left(b/ T^{1/4}\right)$$

(2.44)

where $b$ is a constant related to the hopping mechanism. At high temperatures the deviations from $T^{1/4}$ occurs, which can be understood in term of inter chain hopping. A carrier trapped in a chain, after detrapping thermally, may drift along the same chain, or may open into an adjacent chain. In amorphous polymers the conduction occurs due to two distinct processes; a temperature dependent trap hopping and cooperatively less temperature dependent interchain hopping in which the carriers hop from chain to chain [86].

If two solids are put in contact, the Fermi levels equalize at the interface, the other energy levels moving to accommodate this. In pure insulator the Fermi level bisects the forbidden band. Impurities may introduce allowed levels into the forbidden band, and this moves the
Fermi level up and down. As the temperature is increased the charge carrier concentration increases strongly with temperature. This dominates the temperature dependence of the conductivity, giving it an Arrhenius-like character. It is difficult to generalize about the temperature dependence of DC conduction whether it is ionic or electronic since so many processes are possible. Ohmic (low field) conduction whether ionic or electronic, gives exponential temperature dependence, given by

\[ J = J_0 \exp \left( \frac{-\Delta E}{kT} \right) \]  

(2.45)

where \( J_0 \) is a constant and \( \Delta E \) is the activation energy for carrier generation. Now

\[ J = Ne\mu \]  

(2.46)

where \( N \) is the number of charge carriers, \( e \) their charge, and \( \mu \) their mobility. With extrinsic ionic conduction, it is the mobility i.e. the activated process, \( \Delta E \) being the energy for the ion to hop. With extrinsic electronic conduction, the electrons may move by hopping. However, if the electronic conduction is by excitation into the conduction band, the production of free electrons, \( n \) not their mobility, \( \mu \) is activated. Whatever the Ohmic mechanism, a \( \log J \) vs. \( 1/T \) plot (Arrhenius plot) will usually exhibit increasing linear slopes (activation energies) as \( T \) is raised [89].

For variable range hopping the electrical conductivity is given by
\[ \sigma_{dc} = \sigma_o \exp \left( \frac{T_o}{T} \right)^{\frac{1}{d+1}} \]  

(2.47)

where “\(d\)” is the dimensionality of transport, \(\sigma_{dc}\) is the conductivity, \(\sigma_o\) is the initial value of conductivity, \(T\) is the absolute temperature and \(T_o\) is the activation energy in terms of temperature.

In bulk material ionic conduction occurs due to the drift of defect under the influence of an applied electric field. The degrees of ionic impurities that may be totally ignored in the context of other properties may have a significant effect on conductivity. A theoretical expression may be derived for the current density,

\[ J = \sinh \left( \frac{ed_aE}{2k_B T} \right) \]  

(2.48)

where \(E\) is the electric field, \(d_a\) is the distance between neighboring potential wells and \(e\) is the electronic charge.

### 2.2.8 The Dielectric Behavior of Polymer

The dielectric behavior of polymer is determined by the charge distribution and also by the statistical thermal motion of polar groups. Evidently the chemical structure is the basic factor; in polymers which have polar bonds in their main chains or in side groups one should aspect high dielectric permittivity [90].

Plasma polymers contain a certain number of polar groups independent of whether the monomer used was polar or nonpolar and that is why they are usually suitable for dielectric relaxation studies [2]. It is much more difficult, however, to relate their dielectric relaxation to segmental motions, simply because their structure is not as well defined as the structure of conventional polymers. Due to their cross-link nature and the consequent insolubility of the polymers, very little is known so far about the structure of plasma polymers. In particular the possible presence of conventional chain sequences (those that contribute to the segmental motions) in the cross-linked network has not been established at all.

There are two major polarization mechanisms in polymeric materials that are studied by dielectric spectroscopy: i. polarization due to charge migration and ii. polarization due to orientation of permanent dipole.

Migration of charges gives rise to conductivity. The measured conductivity encompasses the contribution of extrinsic migrating charges (e.g. ionic impurities) and intrinsic migrating charges (e.g. photon transfers along H bonds). Extrinsic conductivity is commonly assumed to be inversely proportional to viscosity according to viscous model for charge transfer.
(Stoke’s law), implying that highly viscous materials should exhibit zero conductivity, which is never the case. This means that the origin of conductivity is highly cross-linked polymer networks should be traces to the intrinsic migrating charges. Different mechanisms of intrinsic charge migration have been proposed but not systematically studied in conjugation with the ongoing chemical reactions in the polymeric materials. While extrinsic conductivity increases during reaction as a result of increase in viscosity, intrinsic conductivity can follow a more complex pattern and hence the trend exhibited by the overall (measured) conductivity will depend on which mechanism (extrinsic or intrinsic) will dominate the dielectric response.

The second major polarization mechanism is dipolar orientation. While electronic or atomic polarization results from induced dipoles, there are many materials that contain permanent dipoles. When such materials are placed in an electric field dipole orientation or dipole polarization is produced as a result of the alignment of dipoles in the direction of the applied field. However unlike the atomic or electronic polarization which is considered instantaneous by dielectric spectroscopy, the orientation (polarization) of permanent dipoles involves cooperative motion of molecular segments with time scales measurable by dielectric spectroscopy. The time dependent loss of orientation of dipoles upon removal of electric field is called dipole relaxation.

There are two additional aspects of induced polarization that one should recognize and account for in the interpretation of experimental results. The first is electrode polarization, which results from accumulation of ions at polymer-electrode interface. The second aspect is the polarization due to the build up of charges at the interface (or in the interface) between components in heterogeneous systems. The polarization is known as interfacial, space charge or Maxwell-Wagner-Sillers.

Some polymers are wholly amorphous and there is only one phase present in the solid material. In such cases there is always a high temperature \( \alpha \)-relaxation associated with the micro-Brownian motion of the whole chains and, in addition, at least one low-temperature (\( \beta, \gamma \), etc.) subsidiary relaxation. The relative strength of the \( \alpha \) and \( \beta \)-dielectric relaxations depends on how much orientation of the dipolar groups can occur through the limited mobility allowed by the \( \beta \)-process before the more difficult but more extensive mobility of the \( \alpha \)-process comes into play there is a partitioning of the total dipolar alignment amongst the molecular rearrangement processes [91].
2.2.8.1 Mechanisms of dielectric polarization

In general the dielectric polarization $P$ may be considered the sum of three contributions,

$$ P = P_e + P_a + P_d $$ (2.49)

Where the subscripts $e$, $a$ and $d$ refer, respectively, to electronic, atomic and dipolar polarization. This provides a basis for the classification of dielectrics into three classes:

(i) Substances for which $P_a = P_d = 0$, so that $P = P_e$

(ii) Substances for which $P_d = 0$, so that $P = P_e + P_a$

(iii) Substances for which all three contributions are different from zero [92].

At the atomic level all matter consists ultimately of positively and negatively charged particles whose charges balance each other macroscopically in the absence of an external electric field giving rise to the overall charge neutrality of the material. Once the electric field is applied the balance of charges is perturbed by the following mechanisms:

**i. Deformation polarization:**

It can be divided into two independent types:

*Electronic polarization*— the displacement of nuclei and electrons in the atom under the influence of an external electric field. As electronic polarization arises from the displacement of the electrons with respect to the atomic nuclei in the applied electric field, electronic polarization is thus an induced polarization effect. Because electrons are very light, they have a rapid response to the field changes; they may even follow the field at optical frequencies.

*Atomic polarization*—the displacement of atoms or atom groups in the molecule under the influence of an external electric field. It is observed when different atoms that comprise a molecule share their electrons asymmetrically and cause the electron cloud to be shifted toward the stronger binding atoms. As a result the atoms acquire charges of opposite polarity and an external field acting on these net charges will tend to displace the equilibrium positions of the atoms themselves.

**ii. Orientational or dipolar polarization:**

In this polarization the electric field tends to direct the permanent dipoles. While electronic or atomic polarization results from induced dipoles, there are many materials that contain permanent dipoles. When such materials are placed in an electric field dipole orientation or dipole polarization is produced as a result of the alignment of dipoles in the direction of the applied field. The rotation is counteracted by the thermal motion of the molecules. Therefore, the dipolar or orientational polarization is strongly dependent on the frequency of
the applied electric field and on the temperature. Like the atomic polarization it is caused by the asymmetric charge distribution between the unlike components of a molecule. However unlike the deformation types of polarization dipolar polarization is created by permanent dipole moments and exists also in the absence of an external field. Such moments experience a torque in an applied field. Fig.2.29 shows that dipoles tend to orient them in the field direction.

![Figure 2.29: Schematic representations of various polarization mechanisms.](image)

iii. Ionic polarization:
In an ionic lattice, the positive ions are displaced in the direction of an applied field while the negative ions are displaced in the opposite direction, giving a resultant dipole moment to the whole body. The ionic polarization demonstrates only weak temperature dependence and is determined mostly by the nature of the interface where the ions can accumulate. Many cooperative processes in heterogeneous systems are connected with ionic polarization.

iv. Space charge polarization:
Space charge polarization is important in dielectric materials which contain charge carriers that can migrate for some distance through the bulk of the material (via, e.g., diffusion, fast ionic conduction, or intercalation), thus creating a macroscopic field distortion. Such a distortion appears to an outside observer as an increase in the capacitance of the sample and may be indistinguishable from a real rise of the dielectric permittivity. Space charge (or interfacial) polarization is the only type of electrical polarization that is accompanied by a
macroscopic charge transport (and in the case when the migrating charge carriers are ions, a macroscopic mass transport as well).

v. Interfacial polarization:
Surfaces, grain boundaries, interphase boundaries (including the surface of precipitates) may be charged, i.e. they contain dipoles which may become oriented to some degree in an external field and thus contribute to the polarization of the material.

To investigate the dependence of the polarization on molecular quantities, it is convenient to assume the polarization $P$ to be divided into two parts: the induced polarization $P_\alpha$, caused by translation effects, and the dipole polarization $P_\mu$, caused by the orientation of the permanent dipoles. In ionic polarization the transport of charge carriers and their trapping can also create induced polarization.

$$ P_\alpha + P_\mu = \varepsilon_0 (\varepsilon - 1) E $$

There are two major groups of dielectrics: polar and nonpolar.

A polar dielectric is one in which the individual molecules possess a permanent dipole moment even in the absence of any applied field; that is, the center of positive charge is displaced from the center of negative charge.

A nonpolar dielectric is one where the molecules possess no dipole moment unless they are subjected to an electric field.

2.2.8.2 Theory of dielectrics
Mostly the dielectric properties are described in terms of the dielectric permittivity (a measure of the ability of a material to be polarized by an electric field) and molecular dipole moments of the substances in local and non-local fields. The dielectric permittivity often called the dielectric constant is a characteristic measurable quantity. The molecular dipole moment measured from the dielectric constant of the bulk material depends on the interaction with its neighbors and hence it gives valuable information about the molecular structure.

A capacitor is a system of two conductors separated by an insulator or vacuum. The two conductors have charges with equal magnitude and opposite sign. The potential difference $V$ between the conductors is proportional to charge, $q$. The ratio of charge to potential difference is called the capacitance, $C$ of the capacitor:

$$ C = \frac{q}{V} $$
In a parallel-plate capacitor separated by a distance $d$, with same area $A$, the uniform electric field between the plates is

$$E = \frac{\sigma_{ac}}{\varepsilon_0}$$

(2.52)

Where $\sigma_{ac}$ is the magnitude of the surface charge density on each plate and $\varepsilon_0$ is the permittivity of the vacuum ($8.85 \times 10^{-12}$ F/m). Then the potential difference between the two plates is

$$V = Ed = \frac{1}{\varepsilon_0} \frac{qd}{A}$$

(2.53)

From Eqn. (2.53) we can see that the capacitance of a parallel-plate capacitor in vacuum is

$$C_0 = \frac{q}{V_0} = \frac{\varepsilon_0 A}{d}$$

(2.54)

When there is a dielectric material between the plates the capacitance $C = \frac{q}{V} = \frac{\varepsilon A}{d}$ (where $\varepsilon$ is the permittivity of the dielectric material) of the capacitor becomes larger than vacuum capacitance $C_0 = \frac{q}{V_0}$.

The ratio of $C$ to $C_0$ is the dielectric constant, $\varepsilon'$ of the material i.e.

$$\varepsilon' = \frac{C}{C_0}$$

(2.55)

Thus it can be written as

$$\varepsilon' = \frac{\varepsilon}{\varepsilon_0}$$

(2.56)

The dielectric constant is therefore also known as the relative permittivity of the material. As, the dielectric constant presents the ratio of the similar type of quantities, it is dimensionless.

A low-$\varepsilon'$ dielectric is a dielectric that has a low permittivity, or low ability to polarize and hold charge. Low-$\varepsilon'$ dielectrics are very good insulators for isolating signal-carrying conductors from each other. Thus, low-k dielectrics are a necessity in very dense multi-layered IC's, wherein coupling between very close metal lines need to be suppressed to prevent a degradation in device performance. A high-$\varepsilon'$ dielectric, on the other hand, has a high permittivity. Because high-$\varepsilon'$ dielectrics are good at holding charge, they are the
preferred dielectric for capacitors. High- \( \varepsilon' \) dielectrics are also used in memory cells that store digital data in the form of charge.

Considering the application of an alternating electrical field, \( E \), amplitude \( E_0 \) and angular frequency \( \omega \), across a dielectric material:

\[
E = E_0 \cos \omega t
\]

This will produce polarization which alternates in direction and, if the frequency is high enough, the orientation of any dipoles which are present will inevitably lag behind the applied field. Mathematically one can express this as a phase lag in the electric displacement:

\[
D = D_0 \cos(\omega t - \delta)
\]

Which may be written

\[
D = D_1 \cos \omega t + D_2 \sin \omega t
\]

Where

\[
D_1 = D_0 \cos \delta \quad \text{and} \quad D_2 = D_0 \sin \delta
\]

This leads to define two dielectric constant

\[
\varepsilon' = \frac{D_1}{\varepsilon_0 E_0} \quad \text{and} \quad \varepsilon'' = \frac{D_2}{\varepsilon_0 E_0}
\]

Linked by the relation

\[
tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\text{Energy dissipated per cycle}}{\text{Energy stored per cycle}}
\]

It is convenient to combine the two quantities into a complex dielectric constant or relative permittivity:

\[
\varepsilon* = \varepsilon' - i \varepsilon''
\]

\( \varepsilon'' \) is called the dielectric loss factor and \( tan \delta \) is usually called the dielectric loss tangent or dissipation factor. \( \varepsilon' \) and \( \varepsilon'' \) are experimentally observable quantities which may be used to characterize the dielectric dispersion over a range of frequencies.

### 2.2.8.3 Dielectric constant

Dielectrics are basically insulating material or a very poor conductor of electric current. When dielectrics are placed in an electric field, no current flows in them as, they have no loosely bound or free electrons that may drift through the material. Instead, electric
polarization occurs. The positive charges within the dielectric are displaced minutely in the
direction of the electric field and the negative charges are displaced minutely in the
direction opposite to the electric field. This slight separation of charge or polarization
reduces the electric field within the dielectric. Dielectric constant is the property of an
electrical insulating material (a dielectric) equal to the ratio of the capacitance of
a capacitor filled with the given material to the capacitance of an identical capacitor in a
vacuum without the dielectric material. The insertion of a dielectric between the plates of,
say, a parallel-plate capacitor always increases its capacitance, or ability to store opposite
charges on each plate, compared with this ability when the plates are separated by a
vacuum. If \( C \) is the value of the capacitance of a capacitor filled with a given dielectric
and \( C_0 \) is the capacitance of an identical capacitor in a vacuum, the dielectric constant, \( \varepsilon' \) is
simply expressed as Eqn. 2.55. Dielectric constant is a number without dimensions. It
denotes a large-scale property of dielectrics without specifying the electrical behaviour on
the atomic scale. The dielectric constant is often called the relative permittivity of a
dielectric material. It is an important parameter in characterizing capacitors. In the
centimeter-gram-second system the dielectric constant is identical to the permittivity.

The relative permittivity of a material under given conditions reflects the extent to which it
concentrates electrostatic lines of flux. In technical terms, it is the ratio of the amount of
electrical energy stored in a material by an applied voltage, relative to that stored in a
vacuum. Likewise, it is also the ratio of the capacitance of a capacitor using that material as
a dielectric, compared to a similar capacitor that has a vacuum as its dielectric. The relative
permittivity of a material for a frequency of zero is known as its static relative
permittivity or its dielectric constant. Other terms used for the zero frequency relative
permittivity include relative dielectric constant and static dielectric constant. While they
remain very common, these terms are ambiguous and have been deprecated by some
standards organizations. The reason for the potential ambiguity is twofold. First, some older
authors used "dielectric constant" or "absolute dielectric constant" for the absolute
permittivity \( \varepsilon \) rather than the relative permittivity. Second, while in most modern usage
"dielectric constant" refers to a relative permittivity, it may be either the static or the
frequency-dependent relative permittivity, depending on context. Relative permittivity is
typically denoted as \( \varepsilon_r(\omega) \) and is defined as

\[
\varepsilon_r(\omega) = \frac{\varepsilon(\omega)}{\varepsilon_0}
\]  
(2.62)
where \( \varepsilon \) is the complex frequency-dependent absolute permittivity of the material, and \( \varepsilon_0 \) is the vacuum permittivity. Relative permittivity is a dimensionless number that is in general complex. The imaginary portion of the permittivity corresponds to a phase shift of the polarization \( P \) relative to electric field \( E \) and leads to the attenuation of electromagnetic waves passing through the medium. By definition, the linear relative permittivity of vacuum is equal to 1 i.e. \( \varepsilon = \varepsilon_0 \).

### 2.2.8.4 Dielectric loss and loss angle

Under a given voltage the dissipation of power in the dielectrics depends on the voltage frequency, the expense of power as an alternating voltage is markedly higher than at direct voltage, and rapidly grows with an increase in frequency, voltage and capacitance and also depends on the material of the dielectric. The amount of power losses in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses or dielectric dissipation factor. When an insulating material is placed between live part and grounded part of electrical equipment, leakage current will flow. As insulating material is dielectric in nature the electric current through the insulation ideally leads the voltage by 90°. Here voltage means the instantaneous voltage between live part and ground of the equipment. But in reality no insulating materials are perfect dielectric in nature. Hence electric current through the insulator will lead the voltage with an angle little bit shorter than 90°. Tangent of the angle by which it is short of 90° is called dielectric dissipation factor or simply \( \tan \delta \). More clearly, the leakage current through an insulation does have two component one is capacitive or reactive and other one is resistive or active. Again it is clear from the diagram, value of \( \delta \) which is also known as loss angle, is smaller, means resistive component of the current \( I_R \) is smaller which indicates high resistive property of the insulating material.

All dielectrics (except vacuum) have two types of losses. One is a conduction loss, representing the flow of actual charge through the dielectric. The other is a dielectric loss due to movement or rotation of the atoms or molecules in an alternating electric field. When the value and direction of the field intensity \( E \) change, the dielectric polarization also varies in value and direction; during one cycle of an alternating field the polarization is established twice and disappears twice. If the dielectric is made up of molecules that are dipoles themselves (polar molecules) or contain weakly bound ions, the orientation or displacement of these particles in an electrical field (orientation polarization) requires a definite time (relaxation time). As a result, the polarization maximum does not occur simultaneously with
the maximum of the field intensity i.e.; there is a phase shift between field intensity and polarization. Because of this there is also a phase difference between the field intensity $E$ and the electrical induction $D$, which causes the energy loss $W$. In a vector representation of the variables, it is possible to say that the electrical induction vector lags behind the electrical field vector by a certain angle $\delta$, which is known as the dielectric loss angle. The loss tangent is the ratio at any particular frequency between the real and imaginary parts of the impedance of the capacitor.

2.2.8.5 Dielectric dispersion

In physics, dielectric dispersion is the dependence of the permittivity of a dielectric material on the frequency of an applied electric field. Because there is always a lag between changes in polarization and changes in an electric field, the permittivity of the dielectric is a complicated, complex-valued function of frequency of the electric field. It is very important for the application of dielectric materials and the analysis of polarization systems.

This is one instance of a general phenomenon known as material dispersion: a frequency-dependent response of a medium for wave propagation.

When the frequency becomes higher:
- it becomes impossible for dipolar polarization to follow the electric field in the microwave region around $10^{10}$ Hz;
- in the infrared or far-infrared region around $10^{13}$ Hz, ionic polarization loses the response to the electric field;
- electronic polarization loses its response in the ultraviolet region around $10^{15}$ Hz.

In the wavelength region below ultraviolet, permittivity approaches the constant $\varepsilon_0$ in every substance, where $\varepsilon_0$ is the permittivity of the free space. Because permittivity indicates the strength of the relation between an electric field and polarization, if a polarization process loses its response, permittivity decreases.

### 2.2.8.6 Dielectric relaxation

Dielectric relaxation is the momentary delay (or lag) in the dielectric constant of a material. This is usually caused by the delay in molecular polarization with respect to a changing electric field in a dielectric medium (e.g. inside capacitors or between two large conducting surfaces). Dielectric relaxation in changing electric fields could be considered analogous to hysteresis in changing magnetic fields (for inductors or transformers). Relaxation in general is a delay or lag in the response of a linear system, and therefore dielectric relaxation is measured relative to the expected linear steady state (equilibrium) dielectric values.

In physics, dielectric relaxation refers to the relaxation response of a dielectric medium to an external electric field of microwave frequencies. This relaxation is often described in terms of permittivity as a function of frequency, which can, for ideal systems, be described by the Debye equation. On the other hand, the distortion related to ionic and electronic polarization shows behavior of the resonance or oscillator type. The character of the distortion process depends on the structure, composition and surroundings of the sample.

**Debye relaxation**

Debye relaxation is the dielectric relaxation response of an ideal, non interacting population of dipoles to an alternating external electric field. It is usually expressed in the complex permittivity $\varepsilon^*$ of a medium as a function of the field's frequency $\omega$.

$$
\varepsilon^*(\omega,T) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + i\omega\tau}
$$

(2.63)
where $\varepsilon_{\infty}$ is the permittivity at the high frequency limit, $\Delta \varepsilon = \varepsilon_s - \varepsilon_{\infty}$ where $\varepsilon_s$ is the static or low frequency permittivity, and $\tau$ is the characteristic relaxation time of the medium. This relaxation model was introduced by and named after the physicist Peter Debye (1913).

### 2.2.8.7 Dielectric polarization in time-dependent electric fields

When an external field is applied to a dielectric, polarization of the material reaches its equilibrium value, not instantaneously but rather over a period of time. By analogy, when the field is suddenly removed, the polarization decay caused by thermal motion follows the same law as the relaxation or decay function of dielectric polarization $\phi(t)$:

$$\phi(t) = \frac{P(t)}{P(0)}$$

(2.64)

where $P(t)$ is a time-dependent polarization vector. The relationship for the dielectric displacement vector $D(t)$ for time-dependent fields may be written as follows:

$$D(t) = \varepsilon_0 \left[ \varepsilon_{\infty} E(t) + \int_{-\infty}^{t} \phi(t') E(t-t') dt' \right]$$

(2.65)

Here $D(t) = \varepsilon_0 E(t)+P(t)$ and $\phi_0$ is the dielectric response function

$$\Phi(t) = (\varepsilon_s - \varepsilon_{\infty}) [1-\phi(t)]$$

where $\varepsilon_s$ and $\varepsilon_{\infty}$ are the low- and high-frequency limits of the dielectric permittivity, respectively. The complex dielectric permittivity $\varepsilon^*(\omega)$ (where $\omega$ is the angular frequency) is connected with the relaxation function by a very simple relationship [6, 11]:

$$\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \hat{L} \left[ -\frac{d}{dt} \phi(t) \right]$$

(2.66)

where $\hat{L}$ is the Laplace transform operator, which is defined for an arbitrary time dependent function $f(t)$ as

$$\hat{L}[f(t)] = f(\omega) = \int_{0}^{\infty} e^{-\omega t} f(t) dt$$

(2.67)

$P=x+i\omega$ where $x \to 0$ and $i$ is an imaginary unit

Eqn. 2.66 gives equivalent information on dielectric relaxation properties of the sample being tested both in frequency and in time domain. Therefore the dielectric response might be measured experimentally as a function of either frequency or time, providing data in the form of a dielectric spectrum $\varepsilon^*(\omega)$ or the macroscopic relaxation function $\phi(t)$. For example, when a macroscopic relaxation function obeys the simple exponential law
\[ \varphi (t) = \exp \left( -\frac{t}{\tau} \right) \]  

(2.68)

where \( \tau \) represents the characteristic relaxation time, the well-known Debye formula for the frequency-dependent dielectric permittivity can be obtained by substitution of Eqn.2.68 into Eqn. 2.66 [32–36, 60]:

\[
\frac{\varepsilon^*(\omega) - \varepsilon_{\infty}}{\varepsilon_s - \varepsilon_{\infty}} = \frac{1}{1 + i\omega\tau_m} 
\]

(2.69)

\[ \varepsilon^*(\omega, T) = \varepsilon' - i\varepsilon'' = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})}{(1 + i\omega\tau)} \]

(2.70)

where \( \varepsilon^* \) is the complex dielectric permittivity, \( \varepsilon' \) is the real part of the complex dielectric permittivity indicates the amount of energy dissipated per cycle, \( \varepsilon'' \) is the imaginary part of the complex dielectric permittivity indicates the amount of energy stored per cycle, \( \varepsilon_s \) is the static or relaxed dielectric constant at \( \omega=0 \) and \( \varepsilon_{\infty} \) is the high frequency or unrelaxed dielectric constant. At low frequencies (\( \omega<<1/\tau \)), dipoles follow the field and under this quasistatic field \( \varepsilon' \approx \varepsilon_s \). As the frequency increases (when, \( \omega<<1/\tau \)), dipoles lag behind the field and \( \varepsilon' \) slightly decreases. At the characteristic frequency (\( \omega=1/\tau \)), the dielectric constant drops (relaxation process), \( \varepsilon'' = 0 \) because this is DC voltage. At very high frequency (\( \omega>>1/\tau \)) dipoles can’t follow the field.

The dielectric constant \( \varepsilon' \) (real part of \( \varepsilon^* \)) is given by

\[
\varepsilon' = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})}{1 + (\omega\tau)^2} 
\]

(2.71)

The imaginary part of \( \varepsilon^* \) is given by

\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_{\infty})\omega\tau}{1 + (\omega\tau)^2} 
\]

(2.72)

The dielectric loss tangent is then expressed as

\[
tag \delta = \frac{\varepsilon''}{\varepsilon'} 
\]

(2.73)

The Eqns. (2.71), (2.72), (2.73) are well-known Debye equations.

An examination of these equations shows the following characteristics:

For small values of \( \omega\tau \) the real part \( \varepsilon' \approx \varepsilon_s \) because of the squared term of the denominator of Eqn 2.71 and \( \varepsilon'' \) is also for the same reason. At \( \omega\tau = 0 \) \( \varepsilon'' = 0 \) because this is DC voltage. Or
very large values of $\omega \tau$, $\varepsilon' = \varepsilon_\infty$, and $\varepsilon''$ is small. For intermediate values of frequencies $\varepsilon''$ is a maximum at some particular value of $\omega \tau$.

The maximum value of $\varepsilon''$ is obtained at a frequency given by

$$\frac{\partial \varepsilon''}{\partial \omega \tau} = (\varepsilon_s - \varepsilon_\infty) \left( \frac{\omega^2 \tau^2 - 1}{1 + \omega^2 \tau^2} \right) = 0$$

Resulting in

$$\omega_p \tau = 1$$

Fig.2.32 Example of the Debye model for the real part (solid line) and imaginary part (dashed line) of the permittivity.

where $\omega_p$ is the frequency at $\varepsilon''_{max}$ corresponding to a critical frequency $\omega_{max} = \frac{1}{\tau}$, and location of this peak provides the relaxation time from the experimental data. For this value of $\omega \tau$ Eqn (2.71) and (2.72) becomes

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)}{2} \text{ and } \varepsilon' = \frac{(\varepsilon_s + \varepsilon_\infty)}{2} \text{ respectively.}$$

The activation energy of the relaxation process can be expressed by the Arrhenius equation:

$$\tau = \frac{1}{2\pi f_{max}} = \tau_0 \exp \left( \frac{\Delta E}{k_B T} \right)$$

Where $f_{max}$ is the frequency of maximum loss at a given temperature, $\tau_0$ is a constant, $T$ is the absolute temperature, and $\Delta E$ can be calculated from the slope of the log $f_{max}$ vs $\frac{1}{T}$, which has a slope $\frac{\Delta E}{2.303 k_B}$. 
It is assumed that the dielectric has average single relaxation time, implies that the charged particle or an ion has two equilibrium position separated by a distance $d$. But in some practical cases the situation is different where dipoles have more than two equilibrium positions. These ideal equations fit well for dilute solutions of large polar molecules. It provides basic understanding of the origin and properties of dielectric spectra. In polymer samples several relaxation processes often exist. There are some cases where the dielectric spectrum can not be explained by Debye equation. This case is handled by some other treatments which are modified Debye relaxation function. The experimental data are better described by nonexponential relaxation laws. This necessitates empirical relationships, which formally take into account the distribution of relaxation times [93].

2.2.8.8 Frequency dependent conductivity

In the polymer material the frequency and temperature dependent conductivity is caused by the hopping of the charge carriers in the localized state and also due to the excitation of charge carriers to upper states in the conduction band. The measured AC conductivity ($\sigma_{ac}$) of conducting and semi-conducting polymers is characterized by the transition above a critical (angular) frequency $\omega_0$ from a low-frequency DC plateau to a dispersive high-frequency region. As an example, the real part of the electrical conductivity $\sigma'$ is plotted as a function of $\omega$ for some conducting polymers and blends. The empirical Jonscher's universal power law [94]:

$$\sigma_{ac} = \sigma(0) + A\omega^n$$

where $\sigma(0)$ is the DC conductivity, $A$ is a constant for a particular temperature and composition, $\omega=2\pi f$ is the angular frequency, the frequency exponent $n$ is a fractional exponent roughly treated as constant $0 < n < 1$, is often used to describe the AC component contributing to the dispersive region. Such behavior is observed in entirely different types of materials, such as disordered semiconductors, polymers, conducting polymer compounds ceramics, ion conducting glasses, heavily doped ionic crystals etc., indicating that the qualitative characteristics of the universal response is irrelevant to the constituting atomic units. It merely has to do with the morphology of the conduction network. Although many different theoretical approaches tried to conclude in a unique fractional exponent value (around 0.7) and justify the empirical universal law of Jonscher, there are serious inefficiencies about the validity of the universal power law:

(a) $n$ can hold values larger than unity (and there is no physical argument to restrict the value of $n$ below 1).
(b) \( n \) is frequency dependent and
(c) what is the upper frequency limit of the 'universal' power law applies [95].

2.2.8.9 Salient features of AC conductivity

Inevitably, measurements of \( \sigma_{ac} \) on variety of disordered solids show universal frequency
dependence characterized by Eqn. 2.77. At low frequency one observe a constant \( \sigma_{ac} \), while
at higher frequencies the \( \sigma_{ac} \) becomes strongly frequency dependent and increases with
frequency. The increase in \( \sigma_{ac} \) usually continues up to phonon frequencies. The following
are the salient features of the \( \sigma_{ac} \) observed in the disordered solids:

a. The real part of \( \sigma_{ac} \) follows an apparent power law behavior \( \sigma_{ac} \propto \omega^n \)
b. The deviation from the power law corresponds to \( n \) increasing weakly with frequency.
c. The frequency exponent \( n \) lies between 0.6 to 1.0.
d. In a fixed frequency range, the exponent \( n \) show a new universality, namely, its
   magnitude increases as temperatures decreases and \( n \to 1.0 \) for \( T \to 0 \)K.
e. When there is no measurable DC conductivity, then \( n \) is close to 1.0.
f. In a log-log representation, the \( \sigma_{ac} \) is much less temperature dependent than that of the DC
   conductivity.
g. When \( n \) close to 1.0, then \( \sigma_{ac} \) is almost temperature independent.
h. Whenever \( \sigma(0) \) is measurable then is a dielectric loss peak.
i. The on set of AC conduction takes place around the dielectric loss peak frequency, \( \omega_p \).
3.1 Introduction

This chapter deals with the plasma polymerization scheme, which includes the details of monomer DEA [(C₆H₅)₂C₆H₃NH₂], substrate, capacitively coupled glow discharge plasma polymerization set up for polymer formation. The optimization for the preparation of PPDEA thin films are examined on the basis of FTIR spectra of PPDEA under different plasma powers and thickness variation on deposition time. The thickness measurement method, doping procedure, contact electrode deposition technique for electrical (DC and AC) measurement of PPDEA thin films, DC and AC measurement set-up and all other characterization instruments and conditions are also included in this chapter.

3.2 The Monomer

The monomer 2, 6 diethylaniline [(C₆H₅)₂C₆H₃NH₂] is manufactured by Aldrich Chemical Company, Germany. The chemical structure of the monomer is shown in Fig.3.1 and its typical properties are stated below:

Table 3.1 General properties of DEA.

<table>
<thead>
<tr>
<th>Form</th>
<th>liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>(C₆H₅)₂C₆H₃NH₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>149.20</td>
</tr>
<tr>
<td>Freezing point</td>
<td>276 K</td>
</tr>
<tr>
<td>Boiling point</td>
<td>516 K</td>
</tr>
</tbody>
</table>

Fig.3.1 The chemical structure of 2, 6 diethylaniline [(C₆H₅)₂C₆H₃NH₂].

2, 6 diethylaniline possesses two ethyl (C₆H₅) groups and one amine (NH₂) group. It is miscible in iso-octane, toluene, ethyl alcohol and 12% in water.

3.3 Substrate Material and its Cleaning Process

The substrates used were precleaned glass slides (25.4 mm X 76.2 mm X 1.2 mm) of Sail Brand, China, purchased from local market. The samples were prepared by depositing the PPDEA thin film and electrodes onto them. To get a homogeneous, smooth and flawless thin polymer film, which is a common property of plasma polymers, it is essential to make
the substrate as clean as possible. The substrates were chemically cleaned by acetone and thoroughly rinsed with distilled water then dried in hot air.

3.4 Capacitively Coupled Plasma Polymerization Setup

A glow discharge is a kind of plasma and the plasma polymerization setup has been used enormously in recent years to form various kinds of plasma polymers. Different configuration of polymerization set up varies the properties of plasma polymers i.e. the geometry of the reaction chamber, position of the electrodes, nature of input power, etc. The glow discharge plasma polymerization setup which was used to deposit the PPDEA thin films consists of the components as shown in Fig.3.2 (a) and (b).

i. Plasma reaction chamber

The glow discharge reactor is made up of a cylindrical Pyrex glass bell-jar having 0.15 m in inner diameter and 0.18 m in length. The top and bottom edges of the glass bell-jar are covered with two rubber L-shaped (height and base 0.015 m, thickness, 0.001 m) gaskets. The cylindrical glass bell jar was placed on the lower flange. The lower flange is well fitted with the diffusion pump by an ‘I’ joint. The upper flange is placed on the top edge of the bell-jar. The flange is made up of brass having 0.01 m in thickness and 0.25 m in diameter. On the upper flange a Laybold pressure gauge head, Edwards high vacuum gas inlet valve and a monomer injection valve are fitted. In the lower flange two highly insulated high voltages feed-through are attached housing screwed copper connectors of 0.01m high and 0.004 m in diameter via Teflon™ insulation.

ii. Electrode system

A capacitively coupled electrode system is used in the system. Two circular stainless steel plates of diameter 0.09 m and thickness of 0.001m are connected to the high voltage copper connectors. The inter-electrode separation can be changed by means of electrode stands and screws. The substrates were kept on the lower electrode for plasma deposition.

iii. Pumping unit

In this system a rotary pump (Vacumbrand GMBH & Co: Germany) is used.

iv. Vacuum pressure gauge

A vacuum pressure gauge head (Laybold AG, Germany) and a gauge meter (ThermotronTM 120) are used to measure inside pressure of the plasma deposition chamber.

v. Input power for plasma generation

The input power supply for plasma excitation comprises of a step-up high-tension
Fig. 3.2 (a) Schematic diagram of the plasma polymerization setup. (1 High voltage power supply, 2 Pirani gage, 3 High tension leads, 4 Gas inlet valve, 5 Gauge head, 6 Monomer injection valve, 7 Flowmeter, 8 monomer container, 9 Pyrex glass cylinder, 10 Stainless steel electrodes, 11 Electrode stands, 12 L-Rubber gasket, 13 Lower flange, 14 Bottom flange, 15 Brass pipe, 16 Vacuum valve, 17 Liquid nitrogen trap, 18 Rotary pump, 19 Switch and 20 Variac.) (b) Plasma polymerization setup in laboratory (c) Plasma polymerization reactor and (d) Glow discharge plasma during deposition.
transformer and a variac. The maximum output of the variac is 220 V and that of the transformer is about 3.5 kV with a maximum current of 100 mA.

vi. Monomer injecting system
The monomer injecting system consists of a conical flask of 25 ml capacity and a Pyrex glass tube with capillarity at the end portion. The capillary portion is well fitted with metallic tube of the nozzle of the high vacuum needle valve.

vii. Flow meter
The system pressure of a gas flow is determined by the feed in rate of a gas and the pumping out rate of a vacuum system. The monomer flow rate is determined by a flow meter. In the plasma polymerization set up a flow meter (Glass Precision Engineering LTD, Meterate, England) is attached between the needle valve and the monomer bottle.

viii. Liquid nitrogen trap
Cold trap, particularly a liquid N\textsubscript{2} trap, acts as a trap pump for different type gas. The liquid N\textsubscript{2} trap system is placed in the fore line of the reactor chamber before the pumping unit in the plasma deposition system. It consists of a cylindrical shape chamber having 6.4 cm diameter and 11.5 cm in length using brass material.

3.5 Generation of Glow Discharge Plasma in The Laboratory
Glow discharges are produced by an applied static or oscillating electric field where energy is transferred to free electrons in vacuum. Inelastic collisions of the energetic free electrons with the gas molecules generate free radicals, ions, and species in electronically excited states. This process also generates more free electrons, which is necessary for a self-sustaining glow. The excited species produced are very active and can react with the surfaces of the reactors as well as themselves in the gas phase. A high-tension transformer along with a variac is connected to the feed-through attached to the lower flange. While increasing the applied voltage, the plasma is produced across the electrodes.

3.6 Deposition of Plasma Polymerized 2, 6 diethylaniline Thin Film
The important feature of glow discharge plasma is the non-equilibrium state of the overall system. In the plasmas considered for the purpose of plasma polymerization, most of the negative charges are electrons and most of the positive charges are ions. Due to large mass difference between electrons and ions, the electrons are very mobile as compared to the nearly stationary positive ions and carry most of the current. Energetic electrons as well as ions, free radicals and vacuum ultraviolet light can possess energies well in excess of the
energy sufficient to break the bonds of typical organic monomer molecules which range from approximately 3 to 10 eV. Some typical energy of plasma species available in glow discharge as well as bond energies encounter at pressure of approximately 1 Pa [4, 96]. In the case of depositing PPDEA thin films, at first, the base pressure of plasma reactor was maintained at about 1.33 Pa and during deposition the chamber pressure was maintained at about 13.3 Pa, by the rotary pump. After finding the desired plasma glow in the reactor the monomer vapor is injected downstream to the primary air glow plasma for some time. Incorporation of monomer vapor changed the usual color of plasma into a light bluish color as shown in Fig.3.2 (d). The substrates used were pre cleaned glass slides of 76.2 mm × 25.4 mm × 1.2 mm (Clear Glass, Sail Brand, China). Prior to thin film deposition, the substrates were chemically cleaned with acetone and rinsed with distilled water in an ultrasonic bath. The cleaned glass slides were then dried in hot air.

3.7 Thickness Measurement Procedure

Thickness is the single most significant film parameter. Any physical quantity related to film thickness can in principle be used to measure the film thickness. It may be measured either by several methods with varying degrees of accuracy. The methods are chosen on the basis of their convenience, simplicity and reliability. Since the film thicknesses are generally of the order of a wavelength of light, various types of optical interference phenomena have been found to be most useful for measurement of film thicknesses. Several of the common methods are i) During Evaporation, ii) Multiple-Beam Interferometry, (Tolansky Fezeau fringes method, Fringes of equal chromatic order, Donaldson method etc.) iii) Michelson interferometer iv) Using a Hysteresis graph and other methods used in film-thickness determination with particular reference to their relative merits and accuracies.

3.7.1 Multiple-Beam Interferometry

This method utilizes the resulting interference effects when two silvered surfaces are brought close together and are subjected to optical radiation. This interference technique, which is of great value in studying surface topology in general, may be applied simply and directly to film-thickness determination. When a wedge of small angle is formed between unsilvered glass plates, which are illuminated by monochromatic light, broad fringes are seen arising from interference between the light beams reflected from the glass on the two sides of the air wedge. At points along the wedge where the path difference is an integral
and odd number of wavelengths, bright and dark fringes occur respectively. If the glass surfaces of the plates are coated with highly reflecting layers, one of which is partially transparent, then the reflected fringe system consists of very fine dark lines against a bright background. A schematic diagram of the multiple-beam interferometer along with a typical pattern of Fizeau fringes from a film step is shown in Fig.3.3. As shown in this figure, the film whose thickness is to be measured is over coated with a silver layer to give a good reflecting surface and a half-silvered microscope slide is laid on top of the film whose thickness is to be determined. A wedge is formed by the two microscope slides, and light multiply reflected between the two silvered surfaces forms an interference pattern with a discontinuity at the film edge as shown in Fig.3.3. A raveling microscope measures the step
height and width of the Fizeau fringes that are formed due to the interference of light reflected from the air/film surface and the film/substrate interfaces, where the optical path difference between successive beams is an integral number of wavelengths. The thickness of the film \( d \) can then be determined by the relation,

\[
d = \frac{\lambda}{2} \frac{b}{a}
\]

where, \( \lambda \) is the wavelength and \( b/a \) is the fractional discontinuity identified in the figure. In conclusion, it might be mentioned that the Tolansky method of film-thickness measurement is the most widely used and in many respects also the most accurate and satisfactory one [97].

### 3.7.2 Measurement procedure of thickness of PPDEA thin film

Multiple-Beam Interferometry technique was employed for the measurement of thickness of the PPDEA thin films. A traveling microscope (Fig.3.4 (a)) along with a monochromatic sodium light is arranged in the laboratory for this purpose. For film thickness measurement a separate glass slide is used in addition to the sample substrates. Two iron disks attached with screws were used for the formation of the wedge of small angle between two glass samples. To generate the step of the PPDEA thin film onto the glass substrate, Teflon tape was used to cover 50% area of the cleaned glass substrate (Fig. 3.4 (b)), which was not exposed to plasma environment during plasma polymerization. After deposition, the Teflon tape was carefully removed from the glass slide and placed under the microscope. The Fizeau fringe pattern (Fig.3.4 (c)) i.e. a step of PPDEA thin film is generated from the surface of the glass slide was used to measure the film thickness. A monochromatic sodium

![Fig.3.4](https://via.placeholder.com/150)

Fig.3.4 (a) Multiple Beam Interferometric set-up in laboratory (b) PPDEA thin film onto glass substrate for thickness measurement (c) Fizeau fringe pattern of PPDEA thin film.
light source of wavelength, $\lambda = 589.30$ nm was used for the measurement of thickness. The thickness of the film “$d$” is determined according to the relation in Eqn 3.1.

### 3.8 Optimization of PPDEA Thin Film Deposition Condition

In order to determine the appropriate experimental parameters that would result in desired deposition of PPDEA thin films, the thickness and FTIR analyses of the thin films deposited at different powers were considered. The FTIR spectra in Fig. 3.5 show that the same vibrational groups are present in all films deposited at different plasma powers. It is evident from Fig. 3.6 that the relative intensity of some absorption bands changes with increasing plasma power. It is observed that the retention of N-H (3400 cm$^{-1}$) and C-H (2900 cm$^{-1}$) bonds decreases with increasing power while the C=C (1400-1500 cm$^{-1}$) bond is retained to a larger extent for 40 W than both of the 50 and 30 W. It is seen from Fig. 3.6 that at 30 W the plasma is low to gain the film thickness properly and at 50 W the plasma is high enough causing slower deposition of the thin films with increasing time due to sputtering. But at 40 W the film thickness increases linearly with deposition time. In view of above observations, PPDEA thin films were prepared at 40 W plasma power for investigation. After attaining the optimized condition for glow discharge the monomer vapor from a monomer container flowed through a fine needle valve attached to the upper flange and connected to a flow meter (Glass Precision Engineering Ltd, Meterate, England) at the flow rate of about 20 cm$^3$/min. The deposition time was varied from 1800 to 5400 sec to get the PPDEA thin films of 100 to 450 nm thick. The optimized conditions of thin film formation for the present study are:

<table>
<thead>
<tr>
<th>Separation between two electrodes</th>
<th>4 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Position of the substrate</td>
<td>Lower electrode</td>
</tr>
<tr>
<td>Deposition voltage</td>
<td>40 W</td>
</tr>
<tr>
<td>Pressure in the reactor before deposition</td>
<td>About 1.33 Pa</td>
</tr>
<tr>
<td>Pressure in the reactor during deposition</td>
<td>About 13.3 Pa</td>
</tr>
<tr>
<td>Flow rate</td>
<td>About 20 cm$^3$/min</td>
</tr>
</tbody>
</table>
Fig. 3.5 The FTIR spectra of PPDEA under 30, 40 and 50 W plasma powers, at 3000 s plasma duration and at the flow rate of about 20 cm$^3$/min.

Fig. 3.6 Deposition time, $t$ vs. thickness, $d$ plots for PPDEA thin films at the flow rate of about 20 cm$^3$/min.
3.9 Experimental techniques for modification of PPDEA thin films

3.9.1 Heat treatment procedure
For SEM, EDX, UV-Vis spectroscopy and FTIR analysis, PPDEA thin films were heat treated (Fig. 3.7 (b)) in air for one hour in a Carbolite furnace (Model: S13-2AU, Bamford, Sheffield, England). The as-deposited thin films were kept in the furnace on a porcelain boat container during heat treatment.

3.9.2 Doping procedure with iodine
The PPDEA thin films were doped by iodine (Iodine resublimed MERCK KGAA, 64271, Darmstadt, Germany) in order to introduce charge carriers into the plasma polymer structure. The samples were doped by placing them in a sealed container containing iodine crystals avoiding a direct contact between the polymer and the dopant. The color of the PPDEA thin films was changed from light to dark brown (Fig. 3.7 (a) and (c)). In the case of electrical measurement the samples were doped by iodine after deposition of the PPDEA thin films on the lower electrode. After doping the sample was brought to the vacuum coating unit for the deposition of upper electrode. The iodine doped PPDEA thin films were subjected to atmospheric conditions at room temperature before and after iodine doping. All the measurements on doped thin films were taken place after storage in air for the same time period.

![Fig. 3.7](image)

Fig. 3.7 (a) as-deposited and (b) heat treated and (c) iodine doped as-deposited PPDEA thin film of 200 nm thick.

3.9.3 Aging procedure
The as-deposited PPDEA thin films of different thicknesses were aged for 180 days in a non-airtight and desiccant free desiccator.
Chapter 3                                                   Experimental Details

3.10 Characterizing Instruments and Measurements

3.10.1 Differential thermal analysis and thermogravimetric analysis
DTA, TGA and DTG of PPDEA were taken in air and nitrogen environment using a computer controlled TG/DTA 6300 system connected to an EXSTAR 6000 station, Seiko Instruments Inc., Japan which is shown in Fig.3.8 (a). The TG/DTA module uses a horizontal system balance mechanism. The heating rate was 10 K/min in air. The PPDEA powder was collected from the substrate surface. During tracing Alumina was used as the reference material.

3.10.2 Differential scanning calorimetry
DSC investigations were performed by using the instrument DSC Q10, TA instruments, USA (Fig.3.8 (b)). For DSC PPDEA was collected from the substrate surface by scrapping method. The DSC operating temperature range was from 220-450 K and at a scan rate of 10 K/min in nitrogen atmosphere.

3.10.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy
The PPDEA thin films were deposited onto small pieces of chemically cleaned glass substrates. To avoid the charging effect the PPDEA films were coated with a thin layer of gold by gold sputtering (AGAR Auto Sputter Coater, M-108A, England) Shown in Fig.3.8 (c). The SEM and EDX were performed by a scanning electron microscope (S-3400 N Hitachi, Japan) which is shown in Fig.3.8 (d). Micrographs were taken at various spots of the samples and at different magnifications.

3.10.4 Fourier transform infrared spectroscopy
FTIR spectroscopic analysis of as-deposited PPDEA at different power and heat treated PPDEA was carried out by a double beam (Shimadzu FTIR-8900, Japan) spectrophotometer which is shown in Fig.3.8 (e) and FTIR spectroscopic analysis of as-deposited and iodine doped as-deposited PPDEA was carried out by a double beam (Shimadzu IR Affinity-1, Japan) spectrophotometer. For FTIR spectroscopic analysis PPDEA was collected from the substrate surface by scrapping method. The sample for FTIR measurements was prepared by potassium bromide (KBr) disk technique. All the spectra were recorded in transmittance mode in the wavenumber range from 4000 to 500 cm$^{-1}$. The FTIR spectrum of DEA liquid monomer was also recorded by putting the liquid monomer in a KBr measuring cell.

3.10.5 Ultraviolet visible absorption spectroscopy
UV-vis spectroscopic analysis was performed by using a dual beam (Shimadzu UV-1601, Japan) UV-vis spectrophotometer which is shown in Fig.3.8 (f). The optical absorption measurement of PPDEA thin films was made in the wavelength range from 270 to 800 nm.
Fig. 3.8 (a) TG/DTA instrument (TG/DTA 6300, Seiko Instruments Inc. Japan) (b) DSC Q 10, TA Instruments (c) Scanning electron microscope (S-3400 N Hitachi, Japan) (d) AGAR auto spatter coater, M-108A, England (e) Double beam FTIR spectrophotometer (Shimadzu FTIR-8900, Japan) (f) Dual beam UV-vis spectrophotometer (Shimadzu UV-1601, Japan).
An uncoated glass substrate made possible a substrate absorption correction. The estimated errors of the optical parameters were calculated by taking the average deviations from the mean (Average deviation = $\frac{1}{n} \sum_{i=1}^{n} d_i$, where $d$ is the deviations and $n$ is the number of deviations) of three samples of each thickness.

**3.10.6 Electrical Measurements**

**3.10.6 (a) Electrode material**

Aluminium (Al) (purity of 4N British Chemical Standard) was used for electrode deposition. Al has been reported to have good adhesion with glass slides. Al film has advantage of easy self-healing burn out of flaws in sandwich structure.

**3.10.6 (b) Electrode deposition**

Electrodes were deposited using an Edward coating unit E-306A (Edward, UK). The system was evacuated by an oil diffusion pump backed by an oil rotary pump. The glass substrates with mask were supported by a metal rod 0.1 m above the tungsten filament. A low-tension power supply of the coating unit was used to heat the filament for the electrode deposition. The low-tension power supply is able to produce 100 A current at a potential drop of 10 V. During evacuation of the chamber by diffusion pump, the diffusion unit was cooled by the flow of chilled water and its outlet temperature was not allowed to rise above 305 K.

![Fig.3.9 Edward coating unit.](image1)

![Fig.3.10. (a) Electrode-sample assembly (b) Al/PPDEA/Al configuration for electrical measurement.](image2)
the penning gauge reads about $1.33 \times 10^{-3}$ Pa, the Al on tungsten filament was heated by low-tension power supply until it was melted. The Al electrode was deposited on to the substrate through a mask by evaporating it from a tungsten filament to form the base electrode in a conventional metal coating unit (Edwards 306, England, UK) (Fig. 3.9) at a pressure of about $1.33 \times 10^{-3}$ Pa. Then PPDEA thin film was deposited on the lower Al electrode through a square shaped mask $(1.5 \times 1.5) \times 10^{-4}$ m$^2$ to form the PPDEA thin film. The substrate was then taken out of the reactor to deposit the upper Al electrode. The electrode-sample assembly of PPDEA thin films is shown in Fig.3.10.

3.10.6 (c) Current density-voltage measurement

The current density-voltage ($J-V$) characteristics of the thin films of different thicknesses were studied in Al/PPDEA/Al and Al/PPDEA (Iodine doped)/Al sandwich configuration

![Diagram of DC electrical measurement](image)

Fig. 3.11 A schematic circuit diagram of DC electrical measurement.

![Arrangement for DC electrical measurement](image)

Fig.3.12 Arrangement for DC electrical measurement
with an effective Al electrode area of $10^{-4}$ m$^2$ at the temperature range from 298 to 373 K. Al (purity 4 N, British chemical standard) was used as the metal electrode. The Al electrode was deposited onto the substrate through a mask by evaporating it from a tungsten filament to form the base electrode in a conventional metal coating unit (Edwards 306, England, UK) at a pressure of about $1.33\times10^{-3}$ Pa. Then PPDEA thin film was deposited on the lower Al electrode through a square shaped mask ($1.5\times1.5$) $10^{-4}$ m$^2$ to form the PPDEA thin film. The substrate was then taken out of the reactor to deposit the upper Al electrode. The current across the thin films was measured by a high impedance electrometer (Keithley, 614, USA) and the DC voltage was supplied step by step by a stabilized DC power supply (Agilent, 6545A, Japan). The DC measurement set up is shown in Fig.3.1. The thermally activated current or the temperature dependence of current across the PPDEA thin films was measured at the applied voltages of 5 and 18 V using the above mentioned electrometer. The measurements were performed from 298 to 423 K. For these measurements the samples were heated by a heating coil which was wrapped around the specimen chamber. The temperature was measured by a Chromel-Alumel (Cr-Al) thermocouple placed very close to the sample which was connected to a digital microvolt (DMV) meter (197 A, Keithley Instruments, USA). The block diagram for DC measurement is shown in Fig.3.1.

3.10.6 (d) AC measurement procedure

The AC capacitance and conductance of pure and iodine doped PPDEA thin films have been measured in the frequency range from 100 Hz to 1 MHz and temperature range from 298 to
373 K using a low frequency impedance analyzer (Agilent 4192 A, Agilent technologies Ltd., Japan). The AC electrical measurement set-up is shown in Fig. 3.13. The AC conductivity, dielectric constant and dielectric loss tangent were calculated from the measured data. Sample temperature was monitored using Cr-Al thermocouple keeping the junction very close to the substrate and connected to a digital microvoltmeter (Keithley, 197A, USA).

3.10.6 (e) Measurements of dielectric properties

The dielectric constant of sample is evaluated from the capacitance measured using equation:

\[
\varepsilon' = \frac{C d}{\varepsilon_0 A}
\]

(3.2)

where \(C\) is the capacitance, \(\varepsilon_0\) is constant of free space \((8.85 \times 10^{-12} \text{ Fm}^{-1})\) \(A\) is the effective cross-sectional area of the electrode and \(d\) is the and thickness of the sample.

The dielectric loss factor, \(\varepsilon''\) can be calculated from measurement value of AC electrical conductance \((G)\) by:

\[
\varepsilon'' = \frac{\sigma_{ac}}{\varepsilon_0 \omega}
\]

(3.3)

where \(\sigma_{ac}\) represents the AC electrical conductivity.

The general formula of \(\sigma_{ac}\) as a function of conductance is given by:

\[
\sigma_{ac} = \frac{G d}{A}
\]

(3.4)

The values of \(\varepsilon'\) and \(\varepsilon''\) or the values of \(G\) and \(C\) can be used to calculate the loss tangent, \(\tan\delta\) using this equation:

\[
\tan\delta = \frac{G}{2\pi fC} = \frac{\varepsilon''}{\varepsilon'}
\]

(3.5)

where \(\delta\) is the phase angle between the electric field and the polarization of the dielectric.

The \(\varepsilon''\) can also be calculated by multiplying the \(\varepsilon'\) with \(\tan\delta\) according to Eqn. 3.5.

The \(\sigma_{ac}\) obeys the empirical universal power law [94]:

\[
\sigma(\omega, t) = \sigma_{dc}(T) + A \omega^n
\]

(3.6)

where \(A\) is dependent on temperature and the exponential factor \(n\) lying between 0 and 1. Neglecting the DC part \(\sigma_{dc}(T)\) in Eqn. 3.6, the value of \(n\) can be determined from the linear slope of the logarithmic plot between \(\sigma(\omega, t)\) and angular frequency \(\omega\).
4.1 Introduction

Plasma polymerization refers to the deposition of films having a broad range of properties by using different monomer gases and different plasma conditions. Therefore much attention has been paid to plasma polymerized thin films, because of their potential as optical and electronic materials. Post deposition modification of plasma polymerized thin films such as heat treatment, aging, doping, etc. may allow diversified application depending on their modifications in various devices. Annealing is a common process which is helpful to influence the structural rearrangement and hence the physical properties of the materials. As the plasma polymerized thin films contain a great concentration of free radicals affecting the changes in the chemical structure (oxidation, bonding of radicals to the polymer chains, etc.), ageing effect of a plasma polymer under ambient conditions should be considered regarding their stability for proper application. The electrical transport properties in the plasma polymerized organic thin films can be modified significantly by introducing charge carriers in the form of extra electrons and/or holes. In this regard iodine plays a significant role as a doping agent in various plasma polymerized thin films [27, 28, 51, 86].

Some experimental data of structural, optical [98] and electrical (DC) [99] studies on as-deposited PPDEA thin films are reproduced in the present study to make some further discussions on their properties and to determine some extended parameters from them. In the present study the thermal and AC electrical properties are observed for as-deposited PPDEA thin films. The values of $\varepsilon'$ observed at different temperatures and different thicknesses are used in the calculation of parameters related to DC conduction mechanisms of as-deposited and iodine doped PPDEA thin films. The thermal, surface morphological, compositional, structural, optical and electrical (AC and DC) properties are observed for modified PPDEA thin films. This chapter includes the study of thermal, surface morphological and chemical characterization of as-deposited, heat treated and iodine doped as-deposited PPDEA thin films by means of DTA, TGA, DTG, DSC, SEM, EDX and FTIR analyses. The optical absorption spectroscopic studies of as-deposited, heat treated, aged and iodine doped as-deposited PPDEA thin films of different thicknesses is analyzed in this chapter from UV-vis spectroscopic analyses. The study on DC and AC electrical properties of as-deposited and iodine doped as-deposited PPDEA thin films are also discussed in this chapter. A comparative analysis between the as-deposited and modified PPDEA thin films are stated on the basis of all the findings from different characterizations.
4.2 Thermogravimetric, Differential Thermal and Differential Thermogravimetric Analyses

The TGA, DTA and DTG were used to characterize the decomposition and the thermal stability of the as-deposited, heat treated and iodine doped as-deposited PPDEA. The analysis was performed in the temperature range of 303 to 973 K and at a scan rate of 10 K/min in air and N\textsubscript{2} environment. The TG, DT and DTG curves for as-deposited, heat treated and iodine doped as-deposited PPDEA are found to be divided into three regions namely A, B and C according to the different stages of thermal changes as shown in Figs. 4.1 to 4.3.

4.2.1 As-deposited PPDEA in air environment

Typical TG, DT and DTG curves of the as-deposited PPDEA in air environment are shown in Figs. 4.1, 4.2 and 4.3 (solid line) respectively. The maximum weight losses in A, B and C regions are about 3%, 4% and 78% respectively and the residue is 15%. The region A corresponds to the 3% weight loss due to exclusion of small amount of the absorbed water in as-deposited PPDEA up to about the water/moisture evolution temperature, T\textsubscript{w} of 367 K. The corresponding DTG trace shows two small peaks in this region due to the evolution of absorbed water in PPDEA. In region B there is a plateau region up to 580 K in TG curve with a weight loss of about 4% which may be due to the removal of unreacted monomer which might settle on the surface of PPDEA. The region C corresponds to the thermal degradation region. However, it is a common practice to consider the degradation temperature at 50% weight loss of the sample as an indicator for structural destabilization \[100\]. The onset temperature of thermal degradation, T\textsubscript{o} is found to be about 580 K. The thermal degradation (50% weight loss) temperature, T\textsubscript{d} of as-deposited PPDEA is observed at 773 K in TG trace. In region C the DT curve shows two endothermic peaks at the temperature of about 608 and 678 K. The two endothermic peaks correspond two-stage degradation event which might have taken place due to the breakdown of C-H, C-N and C=C bonds, and evolution of low molecular weight hydrocarbon and/or N containing compounds. The corresponding DTG trace indicates the same phenomenon by a broad peak. Thus, it can be inferred that as-deposited PPDEA is thermally stable up to about 580 K.

4.2.2 As-deposited PPDEA in nitrogen gas environment

Figs. 4.1, 4.2 and 4.3 (dashed-dotted line) shows the TG, DT and DTG curves respectively of the as-deposited PPDEA in N\textsubscript{2} environment. The TG curves show that the maximum weight losses in A, B and C regions are about 3%, 2% and 41% respectively and the residue
is 54%. In region A the exclusion of small amount of the absorbed water from as-deposited PPDEA is possibly identified by 3% weight loss and up to the $T_w$ of about 364 K. The corresponding DT and DTG traces show a small peak in this region due to the evolution of absorbed water in PPDEA. Region B represents a plateau region up to about 500 K in TG curve with a weight loss of about 2% which may be due to the removal of unreacted monomer settled on the surface of PPDEA. In region C the thermal degradation of as-deposited PPDEA takes place as a large weight loss of about 41% with the $T_o$ of 500 K and no thermal degradation i.e. 50% weight loss is observed for as-deposited PPDEA in $N_2$ environment. The corresponding DT and DTG traces indicate the same phenomenon by a broad peak. In region C, a broad exothermic peak has taken place which might have occurred due to the breakdown of C-H, C-N and C=C bonds, and evolution of low molecular weight hydrocarbon and/or N containing compounds. Thus, it can be inferred that the as-deposited PPDEA is thermally stable in $N_2$ environment up to about 500 K.

4.2.3 Heat treated PPDEA in air environment

For heat treated (at 573 K) PPDEA the typical TG, DT and DTG curves (dotted line) are shown in Figs. 4.1, 4.2 and 4.3 respectively. The maximum three stage weight loss in A, B and C regions is about 5%, 1% and 67% respectively and the residue is 27%. In region A the 5% weight loss at the respective $T_w$ up to 365 K may be due to the exclusion of small amount of water which is inherent due to water absorption in heat treated PPDEA and correspondingly the DTG trace shows one small peak in this region. The region B shows a plateau region up to about 626 K in TG curve without any significant weight loss. In region C the $T_o$ is observed at about 626 K and ends at about 845 K with a large weight loss of 67% in TG trace and the corresponding DTG trace indicates the same phenomenon by a broad peak. The $T_d$ is observed at about 780 K. The degradation event has taken place in the heat treated PPDEA to a higher temperature than that of as-deposited PPDEA due to the fact that heat treatment might have decomposed the loosely bound elements and have strengthened the bonds or generated conjugation in PPDEA. The presence of conjugation in the structure of PPDEA due to heat treatment are discussed in the structural analyses of heat treated PPDEA. In region C, degradation event might have taken place through further breakdown of C-H, C-N and C=C bonds, and removal of low molecular weight hydrocarbon and/or N containing compounds from the bonds. The DT curve also represents
a broad exothermic peak from about 573 to 758 K in C region. Thus, from above discussion it indicates that the heat treated (at 573 K) PPDEA is thermally stable up to about 626 K.

4.2.4 Iodine doped as-deposited PPDEA in air environment

The thermal analyses of TG, DT and DTG are performed for the iodine doped as-deposited PPDEA and the typical traces of them are presented in Figs. 4.1, 4.2 and 4.3 (dashed line) respectively. The thermal traces of iodine doped as-deposited PPDEA also shows three stage weight loss. The maximum weight loss in A, B and C regions is found about 5%, 6% and 77% respectively and the residue is 12%. In TG curve the region A shows $T_w$ up to about 367 K and the region B shows $T_s$ up to 580 K, causing a weight loss a little bit higher than the as-deposited PPDEA. This may be due to the removal of small amount of iodine along with the small amount of water from iodine doped as-deposited PPDEA. In this region an endothermic peak in DT trace is observed correspondingly. The region C showed a large weight loss of about 77%. The $T_o$ of iodine doped as-deposited PPDEA is observed at 580 K. The $T_d$ is found at about 726 K which is lower than the as-deposited one. This corresponds to the evolution of iodine from PPDEA in lower $T_d$. In region C the degradation might have occurred due to the breakdown of C-H, C-N and C=C bonds, and removal of low molecular weight hydrocarbon and/or N containing compounds accompanied with the removal of iodine. Thus, it can be inferred that the iodine doped as-deposited PPDEA is thermally stable up to about 580 K as observed for as-deposited PPDEA.

Table 4.1: TG and DT analyses of as-deposited, heat treated (at 573 K) and iodine doped as-deposited PPDEA thin films.

<table>
<thead>
<tr>
<th>PPDEA</th>
<th>DT Temperature, $T$ (K)</th>
<th>TG Wt % Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_w$</td>
<td>$T_o$</td>
</tr>
<tr>
<td>As-deposited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>367</td>
<td>580</td>
</tr>
<tr>
<td>$N_2$</td>
<td>364</td>
<td>500</td>
</tr>
<tr>
<td>Heat treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>365</td>
<td>626</td>
</tr>
<tr>
<td>Iodine doped</td>
<td></td>
<td></td>
</tr>
<tr>
<td>as-deposited</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>367</td>
<td>580</td>
</tr>
</tbody>
</table>
Fig. 4.1 The TG traces of as-deposited, heat treated and iodine doped as-deposited PPDEA in air and as-deposited PPDEA in N\textsubscript{2} environment.

Fig. 4.2 The DT traces of as-deposited, heat treated and iodine doped as-deposited PPDEA in air and as-deposited PPDEA in N\textsubscript{2} environment.
4.3 Differential Scanning Calorimetry

The DSC was used to characterize the $T_g$ of the as-deposited and heat treated PPDEA (at 473K). The analysis was performed in the temperature range of 220 to 450 K and at a scan rate of 10 K/min in N$_2$ atmosphere. In this experiment the masses of as-deposited and heat treated PPDEA were about $8.2 \times 10^{-3}$ and $8.1 \times 10^{-3}$ kg respectively.

Fig.4.4. The DSC thermograms of (a) as-deposited and (b) heat treated PPDEA
The $T_g$ and $\Delta C_p$ of $T_g$ is calculated according to the procedure stated in section 2.3.2.2. In as-deposited PPDEA there is a step in the curve at about 274 K and may be the $T_g$ point due to glass transition which is about 275 K. In the DSC experiment, $T_g$ is manifested by a step-wise change in the base line, indicating a change in the heat capacity, $\Delta C_p$ of the polymer. The $\Delta C_p$ of as-deposited PPDEA thin film is calculated out to be about 121.8 J/kg-K. After that there is a broad endothermic peak at about 334 K with an onset temperature of 296 K. This transition may involve the ice melting and evolution phenomenon of the small amount of absorbed water inherent in PPDEA in the lower and higher temperature region of the broad peak respectively.

In heat treated PPDEA the $T_g$ is found about 290 K and the $\Delta C_p$ is calculated out to be about 357 J/kg-K. The values of $T_g$ and $\Delta C_p$ of heat treated PPDEA are found to be slightly higher than those of as-deposited PPDEA. The higher value of $T_g$ and $\Delta C_p$ may occur due to the structural rearrangement and/or conjugation resulted by heat treatment which is discussed in the structural analyses of PPDEA. After that there is a sharp endothermic peak at about 335 K with an onset temperature of 331 K. The sharp fall may indicate the presence of conjugation in the structure of PPDEA due to heat treatment. The presence of conjugation will be investigated in the structural analyses of heat treated PPDEA. The broadness of the ice melting and evolution curve is reduced, probably due to the evolution of lower amount of the absorbed water from the heat treated PPDEA.

### 4.4 Scanning Electron Microscopy

The SEM micrographs of thin films of as-deposited PPDEA thin films of different thicknesses were taken in two magnifications (500 and 35000×) and are shown in Fig.4.5 (a) and (b) [99]. The cross-section image in Fig.4.5 (c) proves the smoothness of PPDEA thin film. The SEM micrograph of heat treated (573 K) PPDEA thin film is shown in Fig.4.6. (a). Smooth, uniform and pinhole free surfaces are observed for as-deposited and heat treated PPDEA thin films of different thicknesses and due to heat treatment up to 573 K (in the region of thermal stability) no significant difference in the surface morphology is noticed in PPDEA thin films of different thicknesses. From Fig.4.6 (b) of iodine doped as-deposited PPDEA thin films of 350 nm thick, it is observed that the iodine doped as-deposited PPDEA has become comparatively smoother than that of the as-deposited one.
Fig. 4.5 SEM micrographs of as-deposited PPDEA thin film of 400 nm thick onto glass substrate (a) magnification 500x and (b) magnification 35000x at the accelerating voltage of 10 kV [98]. (c) Cross-section image of PPDEA thin film onto glass substrate.

Fig. 4.6 SEM micrographs of modified PPDEA thin films onto glass substrate (a) PPDEA thin film heat treated at 573 K ($d = 350$ nm) and (b) iodine doped as-deposited (doped for 1 hour) PPDEA thin films onto glass substrate (magnification 500x).
4.5 Energy Dispersive X-ray Analyses

The qualitative compositional analysis is performed by EDX for the same samples used in SEM. The spectrum of EDX is shown in Fig. 4.7. The weight percentages (Wt %) of DEA (calculated), as-deposited, heat treated and iodine doped as-deposited PPDEA thin films are tabulated in Table 4.2. The observations indicate the presence of carbon (C), N and undesired O in all three types of samples and in addition iodine is detected in iodine doped as-deposited PPDEA thin films. The main obstacle of EDX is that it cannot detect the presence of H. But as the DEA contains H, PPDEA thin films should also contain H in it. The presence of O in as-deposited [99] heat treated and iodine doped as-deposited PPDEA thin films implies formation of carbonyl or hydroxyl groups through the reaction of the free radicals with O in the chamber during plasma polymerization and also after the exposure to the atmosphere and these phenomena are believed to occur in plasma polymers [3]. From Table 4.2 it can be predicted that the PPDEA thin films are deficient in C and N with respect to the monomer, which may be due to the breakdown of bonds owing to the complex reaction during plasma polymerization. The reduction in the Wt % of O and N and the increase in the Wt % of C in heat treated PPDEA compared to those of as-deposited PPDEA may be attributed to evolution of O, H and N from PPDEA as a result of structural rearrangement during heat treatment. From Table 4.2 it is observed that the iodine doped as-deposited PPDEA thin film contains C, N, O and iodine in it. The decrease in Wt % of C, the increase in Wt % of O and the presence of iodine implies possible formation of charge transfer complex in PPDEA thin film.

Table 4.2: Wt % of as-deposited, heat treated (at 573 K) and iodine doped as-deposited PPDEA thin films.

<table>
<thead>
<tr>
<th>Elements detected</th>
<th>Monomer (DEA) (calculated) (Wt %)</th>
<th>As-deposited PPDEA thin film (Wt %)</th>
<th>Heat treated PPDEA thin film (Wt %)</th>
<th>Iodine doped as-deposited PPDEA thin film (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>80.5</td>
<td>79.27</td>
<td>86.50</td>
<td>36.66</td>
</tr>
<tr>
<td>N</td>
<td>9.50</td>
<td>8.51</td>
<td>4.95</td>
<td>8.22</td>
</tr>
<tr>
<td>H</td>
<td>10.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>12.22</td>
<td>8.55</td>
<td>44.92</td>
</tr>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10.20</td>
</tr>
</tbody>
</table>
Fig. 4.7 EDX spectra of (a) as-deposited (b) heat treated (at 573 K) and (c) iodine doped as-deposited PPDEA thin films.
4.6 Fourier Transform Infrared Spectroscopic Analyses

4.6.1. DEA and as-deposited PPDEA

The FTIR spectrum of DEA and a representative FTIR spectrum of PPDEA of 200 nm thick are shown in Fig 4.8. In the spectrum of DEA the weak absorption peak at about 3490 and that at about 3395 cm\(^{-1}\) indicates N-H asymmetric and symmetric stretching of a primary amine respectively [73]. In the spectrum of PPDEA these two bands i.e. N-H asymmetric and symmetric stretching become wide and are reduced in intensity at about 3364 and 3190 cm\(^{-1}\) respectively. The reduction of the multiple bands to a single wide band is indicative of monomer fragmentation during plasma polymerization. A shoulder band at about 1620 cm\(^{-1}\) appeared in the low frequency side of N-H stretching band, arising from the overtone of N-H bending (scissoring) vibration [73] in DEA and for PPDEA the band becomes broader and slightly shifted towards higher wavenumber at about 1627 cm\(^{-1}\). Liquid samples of primary amine display medium to strong broad absorption in the 909-666 cm\(^{-1}\) region of the spectrum arising from N-H wagging [73], which is observed in DEA at about 745 cm\(^{-1}\) and is also present in PPDEA in reduced form at 730 cm\(^{-1}\). Multiple bands at 2964 and 2871 cm\(^{-1}\) correspond to the asymmetrical and symmetrical C-H stretching vibrations respectively for CH\(_3\) in DEA which are observed in reduced form at 2960 and 2860 cm\(^{-1}\) in PPDEA. The band at 2934 cm\(^{-1}\) corresponds to the asymmetrical C-H stretching vibration for CH\(_2\) (methylene) in DEA, and is retained in reduced form at 2926 cm\(^{-1}\) in PPDEA. The overtone bands are observed at around 1900-1800 cm\(^{-1}\) in DEA and are also present in PPDEA. The DEA shows a CO\(_2\) impurity band at around 2223 cm\(^{-1}\) which becomes prominent in PPDEA. The C=O asymmetric stretching may be identified in the wide band at around 1800-1600 cm\(^{-1}\) in PPDEA. This indicates the trapped free radicals remaining in the PPDEA which incurs oxidation reactions with molecular O and water vapor during deposition and/or after exposed to air environment [4]. The C=C stretching of benzenoid rings at 1544 cm\(^{-1}\) and quinoid rings at 1456 cm\(^{-1}\) are appeared in DEA and are also present in PPDEA at 1558 and 1470 cm\(^{-1}\) respectively in broad and reduced form. The band at 1456 cm\(^{-1}\) in DEA and the band at 1470 cm\(^{-1}\) in PPDEA can also correspond to the overlapping of CH\(_3\) asymmetrical bending and CH\(_2\) scissoring bands, as, the overlapping of CH\(_3\) asymmetrical bending and CH\(_2\) scissoring bands are generally observed at 1460-1467 cm\(^{-1}\) [74]. The small band at around 1375 cm\(^{-1}\) in DEA is attributed to the symmetric CH\(_3\) bending vibration, which is present in reduced form in PPDEA at 1380 cm\(^{-1}\). When an aromatic ring is present, two bands are observed; a high frequency band (1360-1250 cm\(^{-1}\)) due to conjugation of the electron pair of the N atom with the ring imparting double band character to the C-N bond.
and a lower frequency band (1250-1020 cm\(^{-1}\)) due to aliphatic C-N stretching [74]. In DEA these higher and lower frequency bands are observed at around 1305 cm\(^{-1}\) and 1267 cm\(^{-1}\) respectively and in PPDEA the high frequency band is diminished and the low frequency band is retained in reduced form at 1250 cm\(^{-1}\). The band at 1305 cm\(^{-1}\) in DEA can also correspond to the overlapping bands due to CH\(_2\) twisting and wagging i.e. these bands are overlapped with the C-N band. In PPDEA these bands (CH\(_2\) twisting and wagging) are merged in the broad band (1260-1130 cm\(^{-1}\)). The bands at around 1166, 1107, 1059 cm\(^{-1}\) may be due to C-H in plane and the bands at 964 and 636 cm\(^{-1}\) due to C-H out of plane bending vibrations of benzenoid rings in DEA. These bands are become broad in PPDEA at around 1150-1000 and 700-600 cm\(^{-1}\). The CH\(_2\) rocking might have overlapped with N-H wagging at 745 and 730 cm\(^{-1}\) in DEA and PPDEA respectively. The position of all the band frequencies and the corresponding vibration modes are listed in Table 4.3. These observations are consistent with those of the plasma polymerization of aniline reported by others [48, 86, 101]. The FTIR characteristic peaks of aniline which are ascertained here for PPDEA are also observed in electrochemically synthesized aniline [102] and aniline/pyrrole polymer films [103]. The C-H bonds for ethyl groups of DEA are also observed in PPDEA.

Fig.4.8. The FTIR spectra of DEA and PPDEA (The spectra are shifted along the y-axis for clarity).
thin films. It is observed that in plasma polymerization of aniline by a pulsed source leads to a better control of the final polymer structure and enables to vary plasma-film chemistry on a large scale [13, 67].

The decrease in intensity of the absorption bands in PPDEA compared to monomer indicates the occurrence of a partial fragmentation of the monomer due to 40 W power of plasma. It is observed that with increasing plasma power, cross-linking density may be generated due to the inelastic collisions with high energy electrons and monomer species which may cause the overlapping of electronic orbitals. This results in formation of more stable (chemically, thermally, etc.) polymers due to cross linked structure thus being a good functional or protective coating [104]. As a result different type of polymer (cross-linked/branched) can be produced compared to other conventional polymers prepared by other methods. In PPDEA most of the absorption peaks are shifted to different wavenumbers in contrast to DEA. The small band merges and forms wide bands indicating structural rearrangement. The reduction in intensity of C-H, C-N and N-H bands indicate that polymerization has taken place through larger breaking of these bonds in plasma phase as a consequence of inelastic collisions with high energy electrons and monomer active species. This may initiate fragmentation/cross-linking in PPDEA. Cross-linking may also occur between different C atoms of the chains and/or C=O can be formed due to the breaking of H and N from C-H and C-N bonds of DEA. The presence of C=O in PPDEA suggests that some of the C atoms are in an oxidized state due to post deposition exposure to air giving rise to O reactions with radical species trapped in the structure of the plasma polymer. The retention of C=C bands in PPDEA suggests that the aromatic ring structure (benzenoid and quinoid rings) of DEA is present in PPDEA. The presence of methyl and methylene bands indicate the presence of ethyl group in PPDEA. The above interpretations reveal that the PPDEA may contain an aromatic ring structure with C-N, C-H and ethyl side groups. The presence of O and deficiency of C and N in PPDEA compared to DEA are also detected by EDX analysis [99].

4.6.2 Heat treated PPDEA

The FTIR spectra of heat treated PPDEA at 473 and 573 K are presented in Fig.4.9 as curves $h_1$ and $h_2$ respectively. In $h_1$ and $h_2$ wide absorption bands are observed at about 3400 and 3475 cm$^{-1}$ respectively for N-H asymmetric stretching and 3170 and 3224 cm$^{-1}$ respectively for N-H symmetric stretching and there is no significant shift of the bands. The shoulder band due to overtone of N-H bending vibration is diminished in $h_1$ and $h_2$. In $h_1$
and \( h_2 \) the band due to N-H bending vibration becomes broader and found to be shifted towards lower wavenumber at about 1608 cm\(^{-1}\). The N-H wagging \[73\] band is observed in \( h_1 \) and \( h_2 \) at 740 and 736 cm\(^{-1}\) respectively. The C-H stretching band is diminished in \( h_1 \) and \( h_2 \) which may be due to the removal of H from C-H bands. The CO\(_2\) impurity absorption is also detected in \( h_1 \) and \( h_2 \). This band becomes sharper as the temperature of heat treatment is increased. The overtone bands of substituted of benzene ring are not present in \( h_1 \) and \( h_2 \). The C=O stretching may be identified in the wide band at around 1800-1600 cm\(^{-1}\) in \( h_1 \) and \( h_2 \). These stretching bands have close regions of absorption, so both the absorptions may overlap \[73\]. The C=C stretching of quinoid rings at 1456 cm\(^{-1}\) and benzenoid rings at 1544 cm\(^{-1}\) are also observed in \( h_1 \) at 1560 and 1440 and in \( h_2 \) at 1560 and 1430 cm\(^{-1}\) respectively. These bands become sharper for \( h_2 \) compared to those in P and \( h_1 \). This indicates increased conjugation on heat treatment. The low frequency aliphatic C-N stretching band is retained in reduced form in \( h_1 \) and \( h_2 \) at 1263 and 1261 cm\(^{-1}\) respectively and that of the high frequency band is diminished. The small band at around 1375 cm\(^{-1}\) is attributed to the symmetric CH\(_3\) bending vibration \[73\], which is present in a reduced form in \( h_1 \) and \( h_2 \) at 1400 and 1410 cm\(^{-1}\) respectively. The bands due to C-H in plane and out of plane bending vibrations of benzenoid rings are significantly reduced and become broad in \( h_1 \) and \( h_2 \) at around 1200-1000 (C-H in plane bending) and 700-600 cm\(^{-1}\) (C-H out of plane bending). The position of band frequencies and corresponding vibration modes are listed in Table 4.3.

![Fig.4.9. The FTIR spectra of PPDEA and PPDEA heat treated at 473 (\( h_1 \)) and 573 K (\( h_2 \)) (The spectra are shifted for clarity).](image-url)
In Fig.4.9 it is observed that most of the absorption peaks of PPDEA are shifted to different wavenumbers after heat treated at different higher temperatures and the intensity of the absorption bands decrease, due to superposition of some bands with the wide absorption bands. The formation of wide bands due to merging of small bands indicate structural rearrangement. The reduction in intensity of C-H bands indicating that polymerization has taken place through exclusion of H and N from C-H and C-N bands and further reduction due to heat treatment signifying the occurrence of further H and N exclusion which may allow the presence of C=C bands as a result of cross-linking between different C atoms in PPDEA structure. The presence of C=O in $h_1$ and $h_2$ suggests that some of the C atoms are in an oxidized state through the post deposition reaction of the free radicals with ambient.

Table 4.3: Assignments of FTIR absorption peaks for DEA, as-deposited and heat treated PPDEA.

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>DEA</th>
<th>As-deposited PPDEA</th>
<th>Heat treated PPDEA 473 K</th>
<th>Heat treated PPDEA 573 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H asymmetric stretching</td>
<td>3490</td>
<td>Merged in broad band 3364</td>
<td>Merged in broad band 3400</td>
<td>Merged in broad band 3475</td>
<td></td>
</tr>
<tr>
<td>N-H symmetric stretching</td>
<td>3395</td>
<td>3190</td>
<td>3170</td>
<td>3224</td>
<td></td>
</tr>
<tr>
<td>C-H stretching for CH$_3$</td>
<td>2964, 2871</td>
<td>2960, 2860</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C-H stretching for CH$_2$</td>
<td>2934</td>
<td>2926</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ impurity band</td>
<td>2223 (weak)</td>
<td>2223</td>
<td>2214</td>
<td>2224</td>
<td></td>
</tr>
<tr>
<td>Overtones</td>
<td>1900-1800</td>
<td>Merged in broad band 1900-1800</td>
<td>Merged in broad band 1900-1800</td>
<td>Merged in broad band 1900-1800</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>-</td>
<td>Merged in broad band 1800-1600</td>
<td>Merged in broad band 1800-1600</td>
<td>Merged in broad band 1800-1600</td>
<td></td>
</tr>
<tr>
<td>N-H bending</td>
<td>1620</td>
<td>1627</td>
<td>1608</td>
<td>1608</td>
<td></td>
</tr>
<tr>
<td>C=C stretching vibration of benzenoid rings</td>
<td>1544</td>
<td>1558</td>
<td>1560</td>
<td>1560</td>
<td></td>
</tr>
<tr>
<td>Overlapping of C=C stretching of quinoid rings, CH$_3$ bending and CH$_2$ Scissoring</td>
<td>1456</td>
<td>1470</td>
<td>1440</td>
<td>1430</td>
<td></td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1305, 1267</td>
<td>1250</td>
<td>1263</td>
<td>1261</td>
<td></td>
</tr>
<tr>
<td>C-H in plane bending vibration of benzenoid rings</td>
<td>1166</td>
<td>Merged in broad band 1200-1000</td>
<td>Merged in broad band 1100-1000</td>
<td>Merged in broad band 1100-1000</td>
<td></td>
</tr>
<tr>
<td>N-H wagging</td>
<td>745</td>
<td>730</td>
<td>740</td>
<td>736</td>
<td></td>
</tr>
<tr>
<td>C-H out of plane bending vibration of benzenoid rings</td>
<td>636</td>
<td>Broad band 700-600</td>
<td>Broad band 669-524</td>
<td>Broad band 653-516</td>
<td></td>
</tr>
</tbody>
</table>
From FTIR analyses the presence of C=O and reduction in intensity of C-N bands in heat treated PPDEA can be substantiated by the results obtained from EDX analyses. The EDX analyses imply the presence of O and also imply the reduction in Wt % of N and increase in Wt % of C in heat treated PPDEA thin films compared to those of as-deposited PPDEA thin films. These changes in the PPDEA structure are consistent with a weight loss of about 4% at around 573 K observed in TGA (Fig.4.1) of as-deposited PPDEA.

4.6.3 Iodine doped as-deposited PPDEA

The FTIR spectrum of iodine doped as-deposited PPDEA is shown in Fig.4.10. The iodine doped as-deposited PPDEA has peaks that are largely similar to those of the as-deposited PPDEA with a few deviations. It can be seen from the spectrum of iodine doped as-deposited PPDEA that there are little increase and/or decrease in the band intensity and shift in few absorption bands compared to the as-deposited one. The C-N stretching band at 1261 cm\(^{-1}\) of as-deposited PPDEA shifted to higher wavenumber of 1274 cm\(^{-1}\). The N-H waging band at 793 cm\(^{-1}\) is reduced and shifted to lower wavenumber of 727 cm\(^{-1}\). The shifts observed in N–H and C–N stretching bands indicate that the iodine atoms might have attached to the amine N sites [105] of PPDEA. A new peak at 1070 cm\(^{-1}\) can be ascribed due to C-O or C-C stretching vibration [73]. The intensity of the bands at 2923, 2954, 1700 cm\(^{-1}\) are increased significantly. The several bands corresponding to C-H in plane bending at 1172, 1131, 1030 cm\(^{-1}\) are shifted to 1163, 1121 and 1020 cm\(^{-1}\) respectively and the C-H out of plane bending band at 669 cm\(^{-1}\) is shifted to 673 cm\(^{-1}\). The position of band frequencies and corresponding vibration modes are listed in Table 4.4. Result of iodine doping on plasma polymerized aniline structure reveals that iodine modified the bond length and facilitates shifting of some bands corresponding to some functional groups [51] along the wavelength axis. Thus from the FTIR analyses it can be inferred that iodine doping effects the structure of PPDEA.
Table 4.4: Assignments of FTIR absorption peaks for as-deposited and iodine doped as-deposited PPDEA.

<table>
<thead>
<tr>
<th>Type of vibration</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>As-deposited PPDEA</th>
<th>Iodine doped as-deposited PPDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H asymmetric stretching</td>
<td>3364</td>
<td>3364</td>
<td></td>
</tr>
<tr>
<td>N-H symmetric stretching</td>
<td>3190</td>
<td>3190</td>
<td></td>
</tr>
<tr>
<td>C-H stretching</td>
<td>2926, 2854</td>
<td>2926, 2854</td>
<td></td>
</tr>
<tr>
<td>CO(_2) impurity band</td>
<td>2218</td>
<td>2218</td>
<td></td>
</tr>
<tr>
<td>Overtones</td>
<td>Merged in broad band</td>
<td>Merged in broad band</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1900-1800</td>
<td>1900-1800</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>1700</td>
<td>1700</td>
<td></td>
</tr>
<tr>
<td>CH(_3) Symmetric bending</td>
<td>1380</td>
<td>1380</td>
<td></td>
</tr>
<tr>
<td>N-H bending</td>
<td>1627</td>
<td>1627</td>
<td></td>
</tr>
<tr>
<td>C=C stretching of benzenoid rings</td>
<td>1560</td>
<td>1560</td>
<td></td>
</tr>
<tr>
<td>C=C stretching of quinoid rings</td>
<td>1458</td>
<td>1458</td>
<td></td>
</tr>
<tr>
<td>C-N stretching</td>
<td>1250</td>
<td>1263</td>
<td></td>
</tr>
<tr>
<td>C-H in plane bending vibration of benzenoid rings</td>
<td>1172, 1131, 1030</td>
<td>1163, 1121, 1020</td>
<td></td>
</tr>
<tr>
<td>C-O or C-C</td>
<td>-</td>
<td>1070</td>
<td></td>
</tr>
<tr>
<td>N-H wagging</td>
<td>793</td>
<td>727</td>
<td></td>
</tr>
<tr>
<td>C-H out of plane bending vibration of benzenoid rings</td>
<td>669</td>
<td>673</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4.10 The FTIR spectra for as-deposited and iodine doped as-deposited PPDEA (The iodine doped as-deposited PPDEA spectrum is shifted downward).
4.7 Ultraviolet-Visible Optical Absorption Spectroscopic Analyses

The optical absorbance spectra were analyzed for the as-deposited, heat treated, iodine doped as-deposited and aged PPDEA thin films of different thicknesses to investigate various optical parameters. The UV-vis absorbance spectra in the wavelength region of 290 to 800 nm are taken for the optical absorption studies.

4.7.1 As-deposited PPDEA

The UV-vis absorbance spectra for the as-deposited PPDEA thin films of thicknesses 100, 150, 200 and 350 nm are presented in Fig. 4.11. From the Fig. 4.11 it is observed that the absorbance intensity increases and broadens with increasing thickness of the PPDEA thin films. The absorption coefficient, $\alpha$, can be determined using the formula in Eqn. 2.14. The plot of $\alpha$, as a function of photon energy, $h\nu$, for PPDEA thin films are shown in Fig. 4.12. The Fig. 4.12 shows exponential falling edges, which is similar to other plasma polymerized organic thin films [7], some non-crystalline materials such as transition metal complexes like Cr III organic thin films [106] and some chalcogenide glasses [94]. This happens may be due to the lack of long-range order or due to the random fluctuations of the internal fields associated with the structural disorder and defects in the thin films. The absorption edge starts increasing around 2 eV and there is a rapid rise in $\alpha$ from 3 eV. It is observed that in the low energy region the curves are non-linear and the edges have an exponential fall for values of $\alpha$ below about $3\times10^4$ cm$^{-1}$ for all thin films. From the plots of Fig. 4.12 it is also clear that the curves have different slopes indicating the presence of different optical transitions in the PPDEA thin films.

The optical transition involved in the films can be determined on the basis of the dependence of $\alpha$ on $h\nu$ by using the Tauc relation of Eqn. 2.15 [107]. The Tauc relation possesses a parameter $n$, connected with distribution of density of states and can assume values of 1/2 and 2 for $E_{g(d)}$ and $E_{g(i)}$ respectively. Thus, the $E_g$ values can be obtained by extrapolating the linear portion of the plots to the intercept in the $h\nu$ axis. The plot of $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ for $E_{g(i)}$ and the plot of $(\alpha h\nu)^{2}$ as a function of $h\nu$ for $E_{g(d)}$ of the thin films of different thicknesses are shown in Fig. 4.13 and Fig. 4.14 respectively. The obtained $E_{g(d)}$ and $E_{g(i)}$ values are given in Table 4.5. The values of $E_{g(d)}$ is about 3.60 eV, which remains almost same for all the thicknesses and that of $E_{g(i)}$ varies from 2.23 to 2.38 eV as the thickness varies from 100 to 350 nm for PPDEA thin films. The increase in $E_{g(i)}$ values with increasing thickness is due to the increase in fragmentation/cross-linking in the bulk of the material, resulting from the impact of plasma on the surface of the thin films.
with plasma duration. In non-crystalline/amorphous materials the physical processes that control the behavior of gap states are structural disorder responsible for the tail states and structural defects in deep states. The defect states/disorder in polymer structure produces localized states in the band structure and consequently decreases the $E_g$. The increase of $E_{g(i)}$ values of PPDEA thin films with increasing thickness can be attributed to the reduction of structural defect states/disorder in the PPDEA thin films with increasing thickness i.e. with plasma duration. Plasma duration is one of the plasma parameters [3]. As, there is a linear growth of the PPDEA thin films with plasma duration in its optimized condition, the defect states are not dominating in the range of film thicknesses used for UV-vis spectroscopy. Thus, it can be assumed that the other plasma parameters can also influence the band structure of the resulting PPDEA thin films.

It is observed that the $E_g$ values of PPDEA thin film are higher compared to those of the PPTMA (another plasma polymerized aniline derivative) thin film [48], though they are prepared in the same plasma condition. The higher values of $E_g$ can be attributed to the difference in substitution of methyl and ethyl groups in the aniline precursor resulting plasma polymerized thin films of different chemical structure. It is observed that PPDEA contains more C-H bands (due to ethyl groups) compared to PPTMA. Thus it can be attributed that both of the monomer structures are retained to some extent even after polymerization and are resulting different $E_g$ values. Kamal and Bhuiyan [12] investigated plasma-polymerized pyrrole (PPPy)-N,N,3,5-tetra-methylaniline bilayer thin films of 500 nm thick. The $E_{g(d)}$ and $E_{g(i)}$ values were found to be about 3.65 and 2.35 eV respectively which were very close to the values obtained for PPDEA thin films. The bilayer film also contains more C-H bands i.e. methylene groups than both of the PPPy and PPTMA thin films. Thus it can be inferred that more C-H bands (due to methylene groups) can enhance the $E_g$ values in plasma polymerized thin films. From the investigation on PPAn thin film of 220 nm thick the $E_{g(i)}$ value was found to be 2.07 eV [108] which is close to the $E_{g(i)}$ value of PPDEA. The $E_{g(d)}$ value of electrochemically polymerized poly (o-toluidine) thin films is found to be 2.52 eV. This value is lower than that of PPDEA thin films. This may be due to the difference in the polymerization process, the chemical structure (one methyl group in ortho position of benzene ring) and the degree of polymerization of the polymer [109]. It is observed that the $E_g$ values of PPDEA thin films lies in the range of $E_g$ values of different plasma polymerized aniline/aniline derivatives due to the ethyl group substituted benzene ring of the precursor.
The spectral dependence of $\alpha$ was studied at photon energies less than the energy gap of the films, i.e. in the region of the so called Urbach spectral tail, which characterizes the slope of the exponential edge and is expressed as Eqn. 2.17. Thus, the plots of $\ln \alpha$ vs $h\nu$ should be linear whose slope gives $E_u$, interpreted as the width of the tails of localized states in $E_g$. An increase in $E_g$ of the amorphous thin films can be explained due to the decrease of the band tails in the gap. The $\ln \alpha$ vs $h\nu$ plots for the thin films of different thicknesses are shown in Fig.4.15 and the corresponding values of $E_u$ are also listed in Table 4.5. It can be noticed that the value of $E_u$, which is the band width of the localized states, slightly decreases as the thickness increases. This behavior is due to decrease in the degree of disorder and decrease in density of defect states (which results in the reduction of tailing of bands). The $\sigma_s$, characterizes the broadening of the optical absorption edge due to electron-phonon or exciton-phonon interactions [110] can be determined by using Eqn 2.18. Taking $T = 298$ K, the calculated $\sigma_s$ values are listed in Table 4.5. The $\sigma_s$ values suggest that the absorption edge changes with increasing thickness of PPDEA thin films.

The extinction coefficient, $K$, is calculated from $\alpha$ using the Eqn 2.19. The variation of $K$ for PPDEA thin films with $h\nu$ is shown in Fig. 4.16. It is seen from the plots that $K$ increases with the increase in $h\nu$ and indicating that the probability of electron transfer across the mobility gap rises with $h\nu$.

<table>
<thead>
<tr>
<th>Film thickness, $d \pm 5$ nm</th>
<th>Direct transition energy gap, $E_{g(d)} \pm 0.01$(eV)</th>
<th>Indirect transition energy gap, $E_{g(i)} \pm 0.01$(eV)</th>
<th>Urbach energy, $E_u \pm 0.01$(eV)</th>
<th>Steepness parameter, $\sigma_s \pm 0.001$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>3.56</td>
<td>2.23</td>
<td>0.60</td>
<td>0.043</td>
</tr>
<tr>
<td>150</td>
<td>3.61</td>
<td>2.28</td>
<td>0.51</td>
<td>0.051</td>
</tr>
<tr>
<td>200</td>
<td>3.60</td>
<td>2.34</td>
<td>0.49</td>
<td>0.052</td>
</tr>
<tr>
<td>350</td>
<td>3.63</td>
<td>2.38</td>
<td>0.47</td>
<td>0.055</td>
</tr>
</tbody>
</table>
Fig. 4.11 Variation of absorbance with wavelength, $\lambda$, for as-deposited PPDEA thin films of different thicknesses.

Fig. 4.12 Plots of absorption co-efficient, $\alpha$, as a function of photon energy, $h\nu$ for as-deposited PPDEA thin films of different thicknesses.
Fig. 4.13 $(\alpha h) \frac{1}{2}$ vs. $h\nu$ curves for as-deposited PPDEA thin films of different thicknesses.

Fig. 4.14 $(\alpha h\nu)^2$ vs. $h\nu$ curves for as-deposited PPDEA thin films of different thicknesses.
Fig. 4.15 The Urbach plots ($\ln \alpha$ vs. $h\nu$ curves) for as-deposited PPDEA thin films of different thicknesses.

Fig. 4.16 Extinction coefficient, $K$, as a function of $h\nu$ for as-deposited PPDEA thin films of different thicknesses.
4.7.2. Heat treated and aged PPDEA

The UV-vis absorption spectra of as-deposited, heat treated (373, 473 and 573 K) and aged (180 days) PPDEA thin films of 100, 200 and 350 nm thick are presented in Figs. 4.17 (a) to (c). It is observed that the overall absorption increases with increasing heat treatment temperature and slightly decreases with aging. The plot of $\alpha$, as a function of photon energy, $h\nu$, for as-deposited, heat treated and aged PPDEA thin films are shown in Fig.4.18 (a) to (c). The figures show exponential falling edges in the lower wavelength region. It is observed that in the lower energy region the curves are non-linear and the edges have an exponential fall for values of $\alpha$ below about $3 \times 10^4$ cm$^{-1}$ for all groups of samples.

The plots of $(\alpha h\nu)^2$ as a function of $h\nu$ and $(\alpha h\nu)^{1/2}$ as a function of $h\nu$ is presented in Fig.4.19 (a) to (c) and Fig.4.20 (a) to (c) respectively. The values of $E_{g(d)}$ and $E_{g(i)}$ obtained for heat treated and aged PPDEA thin films of different thicknesses are included in Table 4.6. In Table 4.6 it is observed that both $E_{g(d)}$ and $E_{g(i)}$ values of PPDEA thin films of different thicknesses decrease with the heat treatment temperature. This may happen due to the structural rearrangement and/or conjugation resulted by heat treatment. From EDX and FTIR analyses it may be attributed that due to the evolution of H and N from C-H and C-N bonds, C=C may arise due to heat treatment. These C=C bonds introduces conjugation in the bulk of the material. It is also observed in Table 4.6 that for heat treated and aged PPDEA thin films, the $E_{g(d)}$ values slightly decrease with increasing thickness. Whereas, the $E_{g(i)}$ values increase. This reversible change in $E_{g(d)}$ and $E_{g(i)}$ values after heat treatment possibly occur due to the temperature dependent dilation of the polymer network structure and the temperature dependent electron-phonon interaction, resulting a shift in the relative position of the conduction and valance bands [112]. As a consequence there may be creation of more sublevels at the ends of valance and conduction bands and therefore, reduces $E_{g(d)}$, while extends $E_{g(i)}$ with increasing thickness. In heat treated PPBMI thin films [11] authors found that both $E_{g(d)}$ and $E_{g(i)}$ values increase with increasing film thickness. This discrepancy in the increasing and decreasing trend of $E_g$ values of PPDEA and PPBMI thin films might happen due to the difference between the chemical structure of PPDEA and PPBMI. From FTIR analyses it is observed that PPDEA possesses the N containing bands like N-H stretching, bending, wagging and C-N stretching while PPBMI possesses only N containing band of C=N bond. It is observed that N plays a significant role in $E_g$ of other plasma polymers [113, 114]. The presence of C=O in heat treated and aged PPDEA thin films may affect on the reduction of $E_{g(d)}$ [115] with increasing film thickness. It is evident that the decreasing trend in $E_g$ values in PPDEA thin films heat treated at 323 K is smaller
than those heat treated at 473 and 573 K. This is because, the structural rearrangement may initiates at 373 K and progresses through H and N evolution up to the thermal stability limit of about 580 K as observed in thermal analyses of PPDEA.

Table 4.6: The Direct ($E_{g(d)}$) and indirect ($E_{g(i)}$) optical transition energy gap of heat treated and aged PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Optical transition energy gap (eV)</th>
<th>Types of PPDEA thin film</th>
<th>Post deposition condition</th>
<th>Film thickness, $d \pm 5$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Direct, $E_{g(d)} \pm 0.01$</td>
<td>Aged</td>
<td>180 days</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>3.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>473</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>573</td>
<td>3.27</td>
</tr>
<tr>
<td>Indirect, $E_{g(i)} \pm 0.01$</td>
<td>Aged</td>
<td>180 days</td>
<td>2.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>373</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>473</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>573</td>
<td>1.26</td>
</tr>
</tbody>
</table>

The $ln\alpha vs \ h\nu$ plots for the heat treated and aged PPDEA thin films of different thicknesses are shown in Fig. 4.21 (a) to (c). The corresponding values of $E_u$ are determined according to Eqn. 2.17 and are listed in Table 4.7. It can be noticed in Table 4.7 that the $E_u$ values of the heat treated and aged PPDEA thin films of different thicknesses decrease compared to the as-deposited PPDEA thin films and also with the increasing heat treatment temperatures. This behavior is most probably due to the decrease in the degree of disorder [116] and decrease in density of defect states (which results in the reduction of tailing of bands) which indicates more structural ordering and therefore the $E_{g(i)}$ values decrease with increasing heat treatment temperature.

The $\sigma_s$ values are calculated from Eqn 2.18 taking $T = 298$ K and are given in Table 4.7. In Table 4.7 the $\sigma_s$ values suggest that the absorption edge changes with the variation in thickness of the heat treated and aged PPDEA thin films.

The $K$ is calculated from Eqn 2.19. The variation of $K$ with $h\nu$ for heat treated and aged PPDEA thin film of 200 nm thick is shown in Fig.4.22. The increase of $K$ with the increase of $h\nu$ indicates that the probability of electron transfer across the mobility gap rises with $h\nu$. 
Table 4.7: Urbach energy, $E_u$ (eV) and Steepness parameter, $\sigma_s$ of heat treated and aged PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Optical parameters</th>
<th>PPDEA thin film</th>
<th>Post deposition condition</th>
<th>Film thickness, $d \pm 5$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urbach energy, $E_u \pm 0.01$ eV</td>
<td>Aged</td>
<td>180 days</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Heat treatment temperature (K)</td>
<td>373</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>0.53</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>0.43</td>
<td>0.38</td>
</tr>
<tr>
<td>Steepness parameter, $\sigma_s \pm 0.001$ eV</td>
<td>Aged</td>
<td>180 days</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Heat treatment temperature (K)</td>
<td>373</td>
<td>0.048</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>0.060</td>
<td>0.068</td>
</tr>
<tr>
<td></td>
<td>573</td>
<td>0.064</td>
<td>0.095</td>
</tr>
</tbody>
</table>
Fig. 4.17 Variation of absorbance with wavelength, \( \lambda \) for as-deposited, heat treated (at 373, 473 and 573 K) and aged (for 180 days) PPDEA thin films of different thicknesses: (a) 100 (b) 200 and (c) 350 nm.
Fig. 4.18 Variation of absorption co-efficient, $\alpha$ with photon energy, $h\nu$ for as-deposited, heat treated (at 373, 473 and 573 K) and aged (for 180 days) PPDEA thin films of different thicknesses: (a) 100 (b) 200 and (c) 350 nm.
Fig. 4.19 $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curves for as-deposited, heat treated (at 373, 473 and 573 K) and aged (for 180 days) PPDEA thin films of different thicknesses: (a) 100 (b) 200 and (c) 350 nm.
Fig. 4.20 \((\alpha h\nu)^2\) vs. \(h\nu\) curves for as-deposited, heat treated (at 373, 473 and 573 K) and aged (for 180 days) PPDEA thin films of different thicknesses: (a) 100 (b) 200 and (c) 350 nm.
Fig. 4.21 The Urbach plots for as-deposited, heat treated (at 373, 473 and 573 K) and aged (for 180 days) PPDEA thin films of different thicknesses: (a) 100 (b) 200 and (c) 350 nm.
4.7.3. Iodine doped as-deposited PPDEA

The UV-vis absorption spectra in the range from 290 to 800 nm of iodine doped as-deposited PPDEA thin films of 100, 150, 200, 350 nm thicknesses are shown in Fig. 4.23. It is observed that after iodine doping into the as-deposited PPDEA thin films, each UV-vis absorption spectrum of different thicknesses show a new shoulder/peak in the higher wavelength side at about 360 nm and the peak at 300 nm of as-deposited PPDEA thin film slightly shifted to the higher wavelength side at about 305 nm. This type of spectral change may occur due to the formation of charge transfer complex resulting from the reaction of acceptor type iodine and donor type PPDEA. Such type of spectral change, i.e. a peak at 356.8 nm aroused due to charge transfer complex formation in iodine doped polyanilinefurfural thin films [57]. Elashmawi et al. [117] reported that the spectrum of the unfilled polyvinylidene fluoride (PVDF) is characterized by a sharp absorption edge at about 248 nm and there are no absorption peaks in the longer wavelengths. Two absorption broad peaks were observed at 286 and 353 nm respectively for iodine doped PVDF. The plots of $\alpha$, as a function of $h\nu$ for iodine doped as-deposited PPDEA thin films are shown in Fig. 4.23. The plots of $(a\nu)^2$ as a function of $h\nu$ and $(a\nu)^{1/2}$ as a function of $h\nu$ is presented in Fig. 4.24 (a) and (b) respectively. The values of $E_{g(d)}$ and $E_{g(t)}$ obtained for iodine doped as-deposited PPDEA thin films of different thicknesses are listed in Table 4.8.
It can be seen that iodine doping considerably decrease the $E_g$ values of PPDEA thin films of different thicknesses. The $E_{g(d)}$ values for as-deposited PPDEA thin films were found to be about $3.6 \pm 0.01$ eV whereas after iodine doping the $E_{g(d)}$ values of different thicknesses are found to be about $2.90 \pm 0.01$ eV. The $E_{g(i)}$ values varied from $2.23$ to $2.38 \pm 0.01$ eV for as-deposited PPDEA thin films of different thicknesses whereas $E_{g(i)}$ values varied from $2.11$ to $2.23 \pm 0.01$ eV for iodine doped as-deposited PPDEA thin films of different thicknesses. It is observed that iodine doping effects/ decreases the $E_{g(d)}$ more than the $E_{g(i)}$. The less change in $E_{g(i)}$ might have occurred because, the localized states are not affected much on iodine doping. Thus it can be inferred that a charge transfer complex resulting from iodine doping initiates a change in the $E_g$ values of PPDEA [86].

The $\ln \alpha$ vs $h\nu$ plots for iodine doped as-deposited PPDEA thin films of different thicknesses are shown in Fig. 4.24 (a). The values of $E_u$ are estimated from Fig. 4.24 (a) according to Eqn. 2.17 and are listed in Table 4.8. It can be noticed that the value of $E_u$, which is the band width of the localized states, slightly decreases as the thickness increases. This behavior may be due to decrease in the degree of disorder and decrease in density of defect states (which results in the reduction of tailing of bands). As a consequence the $E_{g(i)}$ values increase with increasing thickness.

The $\sigma_s$ values are calculated from Eqn 2.18 taking $T = 298$ K and are documented in Table 4.8. In Table 4.8 the $\sigma_s$ values suggest that the absorption edge changes with the variation of thickness of iodine doped as-deposited PPDEA thin films. The $K$ is calculated from Eqn 2.19. The $K$ vs. $h\nu$ of iodine doped as-deposited PPDEA thin films of different thicknesses are plotted in Fig.4.24 (b).

### Table 4.8: The optical parameters of iodine doped as-deposited PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Film thickness, $d \pm 5$ nm</th>
<th>Direct transition energy gap, $E_{g(d)}$ (eV) ± 0.01</th>
<th>Indirect transition energy gap, $E_{g(i)}$ (eV) ± 0.01</th>
<th>Urbach energy, $E_u$ (eV) ± 0.01</th>
<th>Steepness parameter, $\sigma_s$ ± 0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.90</td>
<td>2.11</td>
<td>0.43</td>
<td>0.060</td>
</tr>
<tr>
<td>150</td>
<td>2.92</td>
<td>2.15</td>
<td>0.41</td>
<td>0.063</td>
</tr>
<tr>
<td>200</td>
<td>2.89</td>
<td>2.18</td>
<td>0.36</td>
<td>0.072</td>
</tr>
<tr>
<td>350</td>
<td>2.91</td>
<td>2.23</td>
<td>0.30</td>
<td>0.086</td>
</tr>
</tbody>
</table>
Fig. 4.23 Variation of (a) absorbance with wavelength, $\lambda$ and (b) absorption co-efficient, $\alpha$ with photon energy, $h\nu$ (c) $(a\nu)^{1/2}$ vs. $h\nu$ curves and (d) $(a\nu)^2$ vs. $h\nu$ curves for iodine doped as-deposited PPDEA thin films of different thicknesses. For iodine doped as-deposited PPDEA thin films of different thicknesses.
4.7.4. Iodine doped as-deposited PPDEA for different doping periods

The UV-vis absorption spectra in the range from 290 to 800 nm is taken for different doping periods (15, 30 and 60 mins) for PPDEA thin film of 150 nm thick. The absorbance and $\alpha$, are shown in Fig.4.25 (a) and (b). It is observed from Fig. 4.25 (a) that the absorption peak increases with increasing doping period and initiating a shoulder/peak on the higher wavelength side. The shoulder/peak also becomes prominent with the extent of doping period indicating increased number of iodine participating in the charge transfer complex formation. The plots of $\alpha$ vs $h\nu$ (Fig. 4.25 (b)) shows that the curves have different slopes indicating the presence of different optical transitions in the PPDEA thin films. The $E_{g(i)}$ and $E_{g(d)}$ values for different doping period are obtained from Fig. 4.25 (c) and (d) respectively and are listed in Table 4.9. It is found that the $E_{g(i)}$ and $E_{g(d)}$ values decrease from 2.15 to 2.05 ± 0.01 eV and 2.92 to 2.86 ± 0.01 eV respectively with the increasing doping period from 15 to 60 min. It is also observed that both $E_{g(i)}$ and $E_{g(d)}$ values decrease significantly after 15 min iodine doping after then the $E_g$ values gradually decrease with the extent of doping period. This means that initially iodine is absorbed to a larger extent in PPDEA thin films and the amount of absorption becomes less with increasing doping period. The decreasing trend of $E_{g(d)}$ with the increasing doping period indicates that $E_g$ values of PPDEA thin films can be decreased/changed by varying the iodine doping period via formation of charge transfer complex. The $E_{g(i)}$ values slightly decrease with increasing...
doping period, indicating generation of sublevels between the conduction and valance band and thus decreasing the \( E_{g(i)} \) values. It is reported that, iodine doping attracts the electrons from the molecular orbital and produces a sublevel gap or additional level in the band structure and due to the incorporation of iodine, the band gap between the \( \pi-\pi^* \) state decreases as a result of increase in the length of the conjugated \( \pi \) system [118]. Sajeev et al. showed a structural ordering induced by iodine doping of the polymers [51].

The \( \ln \alpha vs h\nu \) plots for iodine doped as-deposited PPDEA thin film of 150 nm thick for different doping periods are shown in Fig. 4.25 (e). According to Eqn. 2.17, the calculated values of \( E_u \) are obtained from the slopes of the Urbach plots and are listed in Table 4.9. It can be noticed that the value of \( E_u \), which is the band width of the localized states decreases as the doping period increases. This behavior is probably due to decrease in the degree of disorder and decrease in density of defect states (which results in the reduction of tailing of bands). Thus it can be attributed that iodine doping reduce the defect states in PPDEA thin films with increasing doping period and therefore increasing the structural ordering and thus decreasing the \( E_{g(i)} \) values with increasing iodine doping period. The \( \sigma_s \) values are calculated from Eqn. 2.18 taking \( T = 298 \) K and are documented in Table 4.9. The \( \sigma_s \) values suggest that the absorption edge changes with the variation of iodine doping period on PPDEA thin films.

Table 4.9: The optical parameters of an iodine doped as-deposited PPDEA thin film (\( d=150 \) nm) for different doping periods.

<table>
<thead>
<tr>
<th>Iodine doping period (min)</th>
<th>Direct transition energy gap, ( E_{g(d)} ) (eV) ± 0.01</th>
<th>Indirect transition energy gap, ( E_{g (i)} ) (eV) ± 0.01</th>
<th>Urbach energy, ( E_u ) (eV) ± 0.01</th>
<th>Steepness parameter, ( \sigma_s ) ± 0.001</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.61</td>
<td>2.28</td>
<td>0.51</td>
<td>0.051</td>
</tr>
<tr>
<td>15</td>
<td>2.92</td>
<td>2.15</td>
<td>0.41</td>
<td>0.063</td>
</tr>
<tr>
<td>30</td>
<td>2.89</td>
<td>2.11</td>
<td>0.37</td>
<td>0.069</td>
</tr>
<tr>
<td>60</td>
<td>2.86</td>
<td>2.05</td>
<td>0.31</td>
<td>0.083</td>
</tr>
</tbody>
</table>
Fig. 4.25 Variation of (a) absorbance (b) absorption coefficient (c) $(\alpha h\nu)^{1/2}$ vs. $h\nu$ curves (d) $(\alpha h\nu)^2$ vs. $h\nu$ curves and (e) Urbach plots ($\ln \alpha$ vs. $h\nu$ curves) for an iodine doped as-deposited PPDEA thin film of 150 nm thick for different doping period.
4.8 Current Density-Voltage Characteristics

4.8.1 As-deposited and iodine doped as-deposited PPDEA thin films

The $J$-$V$ characteristics of thin films of different thicknesses (150, 200, 350 and 450 nm) were studied in Al/PPDEA/Al sandwich configuration, in the voltage range of 0.10 – 20.00 V in the temperatures of 298, 323, 348, 373 and 398 K. The observed $J$-$V$ characteristics of the as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses at room temperature are presented in Fig. 4.26 and as-deposited PPDEA of 350 nm thickness at different temperatures and that of iodine doped as-deposited PPDEA thin films of different thicknesses are shown in Fig. 4.27 and Fig. 4.28 respectively. For both of the as-deposited and iodine doped as-deposited PPDEA thin films it is observed that $J$ increases with decreasing thickness due to increased resistance with increasing thickness. It is also observed that $J$ increases with increasing temperature which may be due to thermally increased molecular motion in the as-deposited and iodine doped as-deposited PPDEA thin films. Each curve of Figs. 4.26 and 4.28 shows two different slopes in the lower and higher voltage regions, corresponding to different conduction processes according to the power law of the form $J \propto V^n$ where $n$ is a power index. The slopes of $0.80 \leq n \leq 0.97$ at the lower voltages indicate approximate Ohmic region while the slopes of $1.70 \leq n \leq 2.83$ at the higher voltages represent the non-Ohmic region of the as-deposited PPDEA thin films of different thicknesses at different temperatures. While for iodine doped as-deposited PPDEA thin films the slopes are found to be about $0.83 \leq n \leq 1.12$ and $1.70 \leq n \leq 9.46$ at the lower and higher voltage regions respectively. The values of the slopes are tabulated in Table. 4.10. Thus it can be inferred that at higher voltage region the iodine doping increased the slope considerably i.e. iodine doping not only increased $J$ value but also increased the rate of the increase of $J$ value at the non Ohmic region. The DC conductivity ($\sigma_{dc}$) vs. $V$ plots for as-deposited and iodine doped as-deposited PPDEA thin films at room temperature are shown in Fig.4.29. It is observed that the $\sigma_{dc}$ of iodine doped as-deposited PPDEA thin film is higher than the as-deposited ones. In the UV-vis spectroscopic analyses it is observed that the $E_g$ values also decrease due to iodine doping. Due to iodine doping the increase in $\sigma_{dc}$ is found more prominent in the non-Ohmic region than that in the Ohmic region of as-deposited PPDEA thin film. This may indicate different type of conduction mechanism in iodine doped as-deposited PPDEA thin films than that operative in as-deposited PPDEA thin films in the non-Ohmic region.
Table 4.10: The slopes in the lower and higher voltage regions at different temperatures for PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Thicknesses of PPDEA thin films $d \pm 5$ (nm)</th>
<th>Measurement temperature (K)</th>
<th>Values of slopes</th>
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<td></td>
<td>As-deposited</td>
<td>Iodine doped as-deposited</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Low voltage region value (Ohmic)</td>
<td>High voltage region value (non Ohmic)</td>
<td>Low voltage region value (Ohmic)</td>
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<tr>
<td>150</td>
<td>298</td>
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</tr>
<tr>
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<tr>
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<td>0.87</td>
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<tr>
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<td>2.39</td>
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<tr>
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Fig. 4.26 $J-V$ plots for (a) as-deposited and (b) iodine doped as-deposited PPDEA thin films of different thicknesses as recorded at room temperature.

Fig. 4.27 $J-V$ plots for as-deposited PPDEA thin film of 350 nm thick at different temperatures.
Fig. 4.28 $J$-$V$ plots for iodine doped as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thick at different temperatures.
The percentages of conductivity increase of iodine doped as-deposited PPDEA thin films than the as-deposited ones were found to be about 190, 122, 110 and 119 % for 150, 200, 350 and 450 nm respectively. Sajeev et al. [51] doped the plasma polymerized aniline thin films by introducing iodine vapor into the plasma polymerization chamber along with the monomer vapor and found the conductivity enhanced by an order of magnitude in the case of both iodine doped RF and AC plasma polymerized thin films. They explained the increase in conductivity due to the fact that the iodine like electron acceptor dopant reduces the binding energy of the polymer. This reduction of binding energy results in an enhanced mobility of the carriers and the conductivity is enhanced further. Adhikari and Banerji [59] synthesized EB-PANI thin films employing thermal evaporation technique and found an increase in electrical conductivity in iodine doped EB-PANI by seven orders of magnitude than the as-deposited EB-PANI. The increase in conductivity is significantly larger than the present case because they have chemically mixed the iodine crystals with EB-PANI. The undoped film showed non-Ohmic behavior whereas the iodine doped films exhibit Ohmic conductivity. Lin and Yuzhong [57] found electrical conductivity of iodine-doped polyanilinefurfural can reach $10^{-3}$ S cm$^{-1}$ which is more than 10 orders of magnitude higher than what was observed at the pristine state. The samples and iodine powder were put in a evacuated and sealed stainless steel container avoiding a direct contact between the polymer and the dopant. The samples approached maximum uptake of iodine in 4 hours. Ameen et al. [119] deposited the undoped and iodine-doped polyaniline on TiO$_2$ thin film using PECVD technique and the iodine-PANI/TiO$_2$ thin film were prepared by the injection of the optimum ethanolic iodine (0.02 M) solution through a syringe into the quartz tube containing the prepared PECVD PANI/TiO$_2$ thin film substrates. Pt/iodine-PANI/TiO$_2$ heterostructure device shows improved I-V properties with considerably high current of 0.05 mA. They attributed that the increase of $J$ might be due to the generation of large number of polarons in the band gap of PANI by iodine doping. It is observed that insitu and long period of iodine doping can yield higher conductivity. As, in the present case the 15 min iodine doping also yielded a small amount of increase in conductivity it can be predicted that a larger increase of conductivity is possible for PPDEA thin films with longer time doping. It is also observed that thinner iodine doped as-deposited PPDEA thin films generate more conductivity than the thicker films. This might have happened because the relative amount of iodine in the thicker films is small.
Fig. 4.29 $\sigma_{dc}$ vs. $V$ plots for as-deposited and iodine doped as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thickness as recorded at room temperature.
Considering PPDEA thin films as insulating thin film, to differentiate the type of conduction mechanisms operative in the thin films, at first the dependence of $J$ on film thickness, $d$, for the samples of different thicknesses of as-deposited and iodine doped as-deposited PPDEA thin films are considered. The thickness dependence of the current follows the relation, $J \propto d^l$ where $l$ is a parameter depending upon the trap distribution. A slope $l < 3$ suggests the possibility of Schottky or PF mechanism and $l > 3$ suggest the possibility of SCLC mechanism. In Fig. 4.30 at the higher voltage of 18 V the dependence of $J$ on as-deposited and iodine doped as-deposited PPDEA thin film of different thicknesses is presented. The linear slopes derived from these plots have yielded negative slopes of about 1.3 and 2.2 for as-deposited and iodine doped as-deposited PPDEA thin films respectively, which are much smaller than that corresponding to SCLC mechanism. These observations do not support the possibility of SCLC mechanism. Thus, it may be inferred that the conduction mechanism operative in these films may either be Schottky or PF. According to Eqn. 2.28, for Schottky or PF mechanism the expression for the current density should give rise to a linear graph if $\ln J$ is plotted against $V^{1/2}$. Plots of $\ln J$ vs $V^{1/2}$ for as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses at different temperatures are shown in Fig. 4.31 and Fig. 4.32 respectively. The plots indicate that $\ln J$ is proportional to $V^{1/2}$ and gives a straight line in the higher voltage region. Thus, it may be inferred that the conduction mechanism in as-deposited and iodine doped as-deposited PPDEA thin films is of Schottky or PF type. For Schottky or PF mechanism it is also necessary that a graph plotted between $\ln J$ vs $d^{1/2}$ should be a straight line with a negative slope [88]. Fig. 4.33 shows that this rule is also satisfied in the case of as-deposited and iodine doped as-deposited PPDEA thin films. Using the slopes of the straight lines of the plots of $\ln J$ vs $V^{1/2}$ the experimental value of the $\beta$ coefficient, $\beta_{exp}$ can be evaluated by Eqn. 2.35 and the theoretical values of $\beta_S$ (Schottky $\beta$ coefficient) and $\beta_{PF}$ (PF $\beta$ coefficient) are calculated from Eqn 2.31 putting the value of high frequency $\varepsilon'$. In Table 4.11 the values of $\beta_{exp}$ are compared with the theoretical $\beta_S$ and $\beta_{PF}$ values. Previously in the $J$-$V$ characteristics of as-deposited PPDEA thin films of 150, 250, 300 and 400 nm thicknesses, the theoretical $\beta_S$ value was calculated by taking the high frequency $\varepsilon'$ of 150 nm PPDEA at room temperature. The $\beta_{exp}$ values of all thickness at different temperatures were found to be close to the theoretical $\beta_S$ value for 150 nm PPDEA at room temperature [99]. From Table 4.11 comparing the values between theoretical and experimental $\beta$ coefficients, it can be attributed that, at all temperatures the as-deposited and iodine doped as-deposited PPDEA has yielded the most probable conduction of different thicknesses as Schottky and
Table 4.11: Experimental and theoretical $\beta$ co-efficients of as-deposited and iodine doped as-deposited PPDEA thin films.

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<th>PPDEA thin film</th>
<th>Film thickness $d \pm 5$ (nm)</th>
<th>Measurement temperature (K)</th>
<th>Dielectric constant, $\varepsilon'$</th>
<th>$\beta$ (eV m$^{1/2}$ V$^{-1/2}$) $\times 10^5$</th>
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<td></td>
<td></td>
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<td>$\beta_{\text{exp}}$</td>
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<td>14.76</td>
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Fig. 4.30 Plots of $J$ vs. $d$ for as-deposited and iodine doped as-deposited PPDEA thin films in the non-Ohmic region (at 18 V).

Fig. 4.31 $\ln J$ vs. $V^{1/2}$ plots for as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thick at different temperatures.
Fig. 4.32 \(\ln J\) vs. \(V^{1/2}\) plots for iodine doped as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thick at different temperatures.

Fig. 4.33 Dependence of \(J\) on \(d^{1/2}\) for as-deposited and iodine doped as-deposited PPDEA thin films at room temperature in the higher voltage region (at 18 V).
PF type respectively. But from the higher temperature measurements, it seems that the $\beta_{\text{exp}}$ value of as-deposited PPDEA gradually increases and approaching towards $\beta_{PF}$ value. The increase in $\beta_{\text{exp}}$ value may be due to trap centers arising possibly from Al diffusion into the PPDEA thin films at high temperature. It may be assumed from $J-V$ characteristics that due to the incorporation of iodine, a charge transfer complex might have formed due to the interaction of donor type PPDEA and acceptor type iodine. The formed charge transfer complex is responsible for the increase in $\sigma_{dc}$. The increase in $\sigma_{dc}$ due to charge transfer complex is reported in the investigations of other plasma polymerized thin films [14, 119]. Due to iodine doping in PPDEA thin films there might have created free charge carriers (electron/holes) which are responsible for PF type conduction in higher voltage region. The overall $J-V$ characteristics through PPDEA thin films can be explained by the fact that for initial voltage bias the cathode is capable of supplying sufficient current to balance that flowing in the insulator, so that the conduction process is Ohmic. There is, however a limit to the current that the cathode can supply that is the saturated thermionic (Richardson) current over the barrier. When this limit is reached, the conduction process is no longer Ohmic in nature. At this stage, because of image force interacting with the electric field at the cathode-insulator interface, the saturation current increases with applied field [89].

### 4.8.2. Schottky barrier height

Schottky emission is a field-assisted thermionic emission that occurs by the transport of electrons, which causes the image force induced lowering potential energy. The potential step changes smoothly at the metal insulator interface. According to Eqn. 2.28, for Schottky type conduction mechanism, a plot of $\ln \left( \frac{J}{T^2} \right)$ versus $(1/T)$ yields a straight line with a slope determined by the permittivity $\varepsilon$ of the insulator. Rearranging Eqn. 2.28 into a relationship between $\ln \left( \frac{J}{T^2} \right)$ and $(1/T)$, can be used to calculate the Schottky barrier height, $\phi_{SBH}$ which is:

$$
\ln \frac{J}{T^2} = \ln A - \frac{1}{kT} \left[ \phi_{SBH} - \beta_s \sqrt{\frac{V}{d}} \right]
$$

(4.1)

Fig. 4.34 illustrates the plots of $\ln \left( \frac{J}{T^2} \right)$ vs. $(1/T)$ for two different bias voltages, which are straight lines. This confirms that the Schottky type conduction mechanism is dominant in PPDEA thin films with Al electrode on both sides. From the slopes of the plots the $e\phi_{SBH}$ is found to ranging from 0.36 to 0.50 eV which are obtained for the voltages of non Ohmic region i.e. at 14 and 18 V for all samples and are documented in Table 4.12. In Table.4.12, it is evident that the changes in values of $\phi_{SBH}$ are very small. The $\phi_{SBH}$ decreases as the bias
voltage increases and is weakly dependent on film thickness. This is probably due to the concentration of impurity or defect states, which takes part in broadening the band gap between the excited states \([107]\), i.e. the \(\varphi_{SBH}\) is weakly dependent on thickness for as-deposited PPDEA thin films. These observations establish that the conduction mechanism in PPDEA thin films is of Schottky type.

Table 4.12: Values of Schottky barrier height, \(e\varphi_{SBH}\) (eV) for as-deposited PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Film thicknesses, (d) (nm)</th>
<th>Schottky barrier height, (e\varphi_{SBH}) (eV) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 V</td>
</tr>
<tr>
<td>150</td>
<td>0.39</td>
</tr>
<tr>
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<td>400</td>
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</table>

![Schottky barrier height graph](image)

Fig.4.34  Temperature dependence of the Schottky emission dominated leakage current of as-deposited PPDEA thin film at different bias voltages \((d = 400\, \text{nm})\).
4.8.3. Temperature dependence of current density

Figs. 4.35 and 4.36 show the dependence of $J$ on inverse absolute temperature, $1/T$, for as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses. There are two curves, one in the Ohmic region with an applied voltage of 5 V, and the other in the Schottky region with an applied voltage of 15 V. It is observed that the current density increases slowly for temperatures <373 K and above this temperature $J$ increases rapidly with temperature. This increase in $J$ with temperature may be due to the increased thermal excitation of the ions and/or electrons in PPDEA thin films. Each of the curves has two different slopes in the low temperature (<373 K) and in the higher temperature (>373 K) region. The activation energies calculated from the slopes of plots of Figs. 4.35 and 4.36 using the Eqn. 2.45 for all samples and are reported in Table 4.13. It is observed from Table 4.13 that for as-deposited PPDEA thin films, lower temperature $\Delta E$ is found to be about $0.093 \pm 0.013$ eV and $0.081 \pm 0.002$ eV for applied voltage of 5V (Ohmic) and 15 V (Schottky) respectively and that at the higher temperature region is $0.91 \pm 0.12$ eV and $0.90 \pm 0.05$ eV for applied voltage of 5V and 15 V respectively. For iodine doped as-deposited PPDEA thin films the lower temperature $\Delta E$ is found to be about $0.055 \pm 0.005$ and $0.068 \pm 0.0075$ eV for 5 and 15 V respectively and those for high temperature is found to be about $0.80 \pm 0.10$ and $0.75 \pm 0.04$ eV for 5 and 15 V respectively. The lower value of $\Delta E$ in low temperature can be attributed to hopping conduction and the higher value of $\Delta E$ in the higher temperature may be due to the distinct energy level transitions. Thus the increasing trend of $\Delta E$ with increasing temperature in as-deposited and iodine doped as-deposited PPDEA thin films may be attributed to a transition from a hopping regime to a regime dominated by distinct energy levels. In this kind of transition process, the localized carrier most possibly bound with the agglomerates itself. As a result the carriers cannot take part in the conduction throughout the bulk of the material at the lower temperature.

The plots of $\Delta E$ vs. $d$ curves for as-deposited and iodine doped as-deposited PPDEA thin films at 5 V (Ohmic region) are shown in Fig 4.37. It is evident from Table 4.13 and Fig. 4.37 that at 5 V (Ohmic region) and in low temperature, the $\Delta E$ for both as-deposited and iodine doped as-deposited PPDEA thin films increases with increasing thickness but in high temperature the $\Delta E$ decreases with increasing thickness. This implies that in low temperature the carriers present in both types of PPDEA thin films are bound by increased agglomerates/crosslinks in higher thickness samples but at higher temperature the increased numbers of carriers in higher thickness samples get thermal excitation energy to sweep over...
Fig. 4.35 Plots of $J$ vs. inverse of absolute temperature for as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thicknesses in Ohmic and non-Ohmic regions.
Fig. 4.36  Plots of $J$ vs. inverse of absolute temperature for iodine doped as-deposited PPDEA thin films of (a) 150 (b) 200 (c) 350 and (d) 450 nm thicknesses in Ohmic and non-Ohmic regions.
the potential barrier and thus reduces the $\Delta E$. But at 15 V (non-Ohmic region) any significant thickness dependence of $\Delta E$ is not observed. It is also observed that the $\Delta E$ of as-deposited PPDEA thin films is higher in all voltage and temperature regions compared to those of the iodine doped as-deposited ones. This may happen due to the charge transfer complex/carrier formation in iodine doped as-deposited PPDEA thin films. The charge transfer complex/carriers provide lower energy to activate the carriers to conduct through the PPDEA thin films.

Table 4.13: Values of activation energy, $\Delta E$ (eV) for as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses.

<table>
<thead>
<tr>
<th>Thickness, $d \pm 5$ (nm)</th>
<th>Temperature region</th>
<th>5 V (Ohmic region)</th>
<th>15 V (non-Ohmic region)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>As-deposited</td>
<td>Iodine doped as-deposited</td>
</tr>
<tr>
<td>150</td>
<td>Low Temperature</td>
<td>0.085</td>
<td>0.048</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>0.094</td>
<td>0.052</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>0.104</td>
<td>0.057</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td>0.106</td>
<td>0.064</td>
</tr>
<tr>
<td>150</td>
<td>High Temperature</td>
<td>1.10</td>
<td>0.83</td>
</tr>
<tr>
<td>200</td>
<td></td>
<td>0.97</td>
<td>0.77</td>
</tr>
<tr>
<td>350</td>
<td></td>
<td>0.81</td>
<td>0.71</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td>0.76</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Fig. 4.37 $\Delta E$ vs. $d$ curves for as-deposited and iodine doped as-deposited PPDEA thin films at 5 V (Ohmic region).
4.9. AC Electrical Properties

4.9.1. Variation of AC conductivity with frequency

The $\sigma_{ac}$ of as-deposited and iodine doped as-deposited PPDEA thin films are calculated from the measured values of $G$ using the expression of Eqn. 3.4. The $\sigma_{ac}$ as a function of frequency at different temperatures (from 298 to 373 K) of as-deposited and iodine doped as-deposited PPDEA thin films are shown in Figs. 4.38 and 4.39 respectively. It is found that $\sigma_{ac}$ increases as frequency increases for all the measurement temperatures. It is also observed that $\sigma_{ac}$ increases more rapidly in the higher frequency region (<10 kHz). This type of behavior can be explained by the relation of Eqn. 2.77, where $n$ is the index that is used to understand the type of conduction/relaxation mechanism dominant in amorphous materials and takes the value less than unity for Debye type mechanism. For as-deposited PPDEA thin films the values of $n$ determined from Figs. 4.38 and 4.39 respectively, are listed in Table 4.14. The values of $n$ are found to lie between 0.73 and 1.21 in the low frequencies ($f<1$kHz) and that for iodine doped as-deposited PPDEA thin films are found to lie between 0.78 and 1.27. In the higher frequency region ($f>1$kHz) for as-deposited PPDEA thin films the value of $n$ are found to lie between 0.92 and 1.77 and that for iodine doped as-deposited PPDEA thin films are found to lie between 1.00 and 1.71. The exponent $n$ is the measure of departure from ideal Debye type of relaxation process. It has been shown that when $n \leq 1$ the polarization process is of Debye-type (the case of nearest-neighbour interacting dipoles). The calculated values of the frequency exponent, $n$ of as-deposited and iodine doped as-deposited PPDEA thin films corresponds to Debye-type in the lower frequency region and in the high frequency region corresponds to the relaxation process other than Debye type. Cvejic et al. [120] reported that the value of exponent $n$ in the region of $0.61 \pm 0.01$ i.e. $n \leq 1$ corresponds to the interfacial polarization. In PPDEA thin films the values of $n$ are also $\leq 1$ in the low frequency regions, probably indicating interfacial polarization. In the higher frequency regions the values of $n$ are found to lie between 1.3 to 1.77, but as the temperature increases the values of $n$ begins to decrease and are found to lie between 0.78 to 1.10. This suggests that as the temperature increases, there is a transition in the polarization process from other than Debye type to Debye type.
Table 4.14: Values of frequency exponent, \( n \) in the low and high frequency regions.

<table>
<thead>
<tr>
<th>Thickness, ( d \pm 5 ) (nm)</th>
<th>Values of “( n )” in the frequency range</th>
<th>As-deposited PPDEA thin films</th>
<th>Iodine doped PPDEA thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measurement Temperatures (K)</td>
<td>10(^2)-10(^3) Hz</td>
<td>&gt;10(^3) Hz</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>0.92</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.04</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.81</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.91</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>1.12</td>
<td>1.01</td>
</tr>
<tr>
<td>150 nm</td>
<td>298</td>
<td>1.19</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.88</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.94</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.73</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>1.21</td>
<td>1.02</td>
</tr>
<tr>
<td>200 nm</td>
<td>298</td>
<td>1.07</td>
<td>1.77</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.98</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.90</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>0.93</td>
<td>1.01</td>
</tr>
<tr>
<td>350 nm</td>
<td>298</td>
<td>1.16</td>
<td>1.73</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>0.94</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>348</td>
<td>0.92</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>373</td>
<td>0.87</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>398</td>
<td>0.93</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Fig. 4.38 Dependence of $\sigma_{ac}$ on frequency measured at different temperatures of as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
Fig.4.39 Dependence of \( \sigma_{ac} \) on frequency measured at different temperatures of iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
4.9.2 Variation of AC conductivity with temperature

The plots of $\sigma_{ac}$ vs. inverse of absolute temperatures ($1/T$) at different frequencies for as-deposited and iodine doped as-deposited PPDEA thin films are shown in Figs. 4.40 and 4.41 respectively. The $\Delta E$ for as-deposited and iodine doped as-deposited PPDEA thin films were determined from the plots of temperature dependence of $\sigma_{ac}$ shown in Figs. 4.40 and 4.41 respectively.

For as-deposited PPDEA thin films it is found that in low temperature and in lower frequencies ($f \leq 5$ kHz) the activation energy is very low which is about 0.005 to 0.064 eV and that for iodine doped as-deposited PPDEA thin films are about 0.015 to 0.079 eV. In higher temperature and in lower frequencies ($f \leq 5$ kHz) the activation energy is found about 0.03 to 0.21 eV and 0.038 to 0.20 eV for as-deposited and iodine doped as-deposited PPDEA thin films respectively. In higher frequency ($f \geq 5$ kHz) no significant temperature dependence of $\sigma_{ac}$ are observed for both as-deposited and iodine doped as-deposited PPDEA thin films. Mathai et al. [31] found a low activation energy of 0.334 to 0.056 eV throughout the whole frequency and temperature range scanned and was stated that the strong dependence of $\sigma_{ac}$ on frequency and the low activation energies of the carriers are indicative of a hopping conduction mechanism in PPPA thin films. In as-deposited PPDEA thin films the values of the activation energy are close to those of the RF PPPA thin films. In PPDEA thin films the $\sigma_{ac}$ also showed good frequency dependence with low activation energy. Thus it can be attributed that the conduction most possibly dominated by hopping of carrier between the localized states in all temperatures in as-deposited and iodine doped as-deposited PPDEA thin films. It is also observed that there are some anomalies of $\sigma_{ac}$ in the lower temperature region. This low temperature anomaly is possibly due to the effect of small amount of absorbed water inherent in PPDEA thin films due to moisture absorption. Many plasma polymerized thin films have a strong affinity of O and moisture [18]. The presence of O in PPDEA thin films also has been detected by EDX analyses.
Fig. 4.40 Variation of $\sigma_{ac}$ as a function of temperatures at different frequencies of as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
Fig. 4.41  Variation of $\sigma_{ac}$ as a function of temperatures at different frequencies of iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
4.9.3 Frequency dependence of dielectric constant

The decrease of $\varepsilon'$ with increasing frequency is the expected behavior in most dielectric materials. This is due to dielectric relaxation which is the cause of anomalous dispersion. From a structural point of view, the dielectric relaxation involves the orientation polarization which in turn depends upon the molecular arrangement of a dielectric material. So, at higher frequencies, the rotational motion of the polar molecules of dielectric is not sufficiently rapid for the attainment of equilibrium with the field, hence $\varepsilon'$ seems to be decreasing with increasing frequency [121].

![Graph](image)

Fig. 4.42. Variation of $\varepsilon'$ with frequency measured at different temperatures for as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
The $\varepsilon'$ of PPDEA thin films of different thickness are calculated by the Eqn.3.2. The variation of $\varepsilon'$ with frequency in the range from 100 Hz to 1 MHz for as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses (150, 200, 350, 450 nm) at different temperatures are shown in Figs.4.42 and 4.43 respectively. Typically, the frequency dependent $\varepsilon'$ in organic polymers is dominated by reorientation of molecular dipoles [122]. It is observed in as-deposited and iodine doped as-deposited PPDEA thin films that, $\varepsilon'$ decreases slowly with increasing frequency at fixed five different temperatures. This type of frequency dependence of $\varepsilon'$ might be attributed to the combination of two
factors reported by Zhao et al. [40]. First, some charges present in the dielectric materials can migrate some distance through the dielectric as an electric field is applied. When such carriers are impeded in their motion, space charge and macroscopic field distortions will result. As the charge carriers migrate under the influence of an electric field, it is possible that they get blocked at the electrode-dielectric interface and leads to interfacial polarization. Such distortion shows an increased value of \( C \) at low frequencies. Second, the plasma deposited film has a high concentration of radicals. The rotation of radicals may result in an increase in the polarization in the low frequency region. As the frequency is raised, the value begins to drop which could be due to lack of response of the dipoles, in other words incapability of the dipole to follow the field variations in the high frequency. Thus, from the above suggestion it can be attributed that the frequency dependence of \( \varepsilon' \) of PPDEA thin films correspond to interfacial and dipolar polarization in the lower and higher frequency regions respectively.

The probable reason for the “switching” in the \( \varepsilon' \) above a frequency of about \( f > 100 \) kHz is most probably due to the inter-electrode tunneling. This type of switching in the \( \varepsilon' \) is also observed in PANI thin films at about \( f = 2 \) MHz [86].

It is observed in Fig.4.44 that the \( \varepsilon' \) values of pure PPDEA thin films increased after iodine doping and this may be attributed to the presence of highly polarizable molecular iodine. It is also observed that the \( \varepsilon' \) of pure and iodine doped PPDEA thin films increases with increasing thickness. Kumar [123] also observed an increase of \( \varepsilon' \) with increasing thickness in plasma polymerized lemongrass oil thin films. In PPDEA thin films some polar groups which can participate in increasing \( \varepsilon' \) may arise due to cross-linking and some cross-linked groups may also act as polar groups. The increase of optical band gaps of PPDEA thin films due to increased cross-linking with increasing thickness i.e. deposition time is reported earlier [99]. Agostino [3] reported that limiting the residence time of molecules in the plasma is one of the inevitable factors to preserve complex monomer structures in the resultant plasma polymers and to vary the cross-link density over a wide range. It is also reported that, as the deposition time increases there is an increase in the temperature of plasma (may be small) with deposition time due to the collision of the energetic species. This temperature may also affect the structure of the plasma polymerized thin film with deposition time. Cho et al. [36] reported that the cross-linking can increase the \( \varepsilon' \) values of the plasma polymerized pure ethylcyclohexane thin films. Wang et al. [124] discussed that polymer possessing a large alkyl side group would have the lower \( \varepsilon' \) value. In the present case as the cross-linking in plasma polymers intends short range order of the polymer chain
which indicates a decrease in alkyl side groups, the $\varepsilon'$ might have increased with increasing cross-linking or increasing thickness of PPDEA thin films. Yuan and Chung [125] studied the cross-linking effect on the dielectric properties of a family of cross-linked polypropylene (x-PP) thin film. Evidently, the butyl styrene cross-linkers increased the $\varepsilon'$. The PPDEA thin films showed a high value of $\varepsilon'$ for each thickness which can be attributed due to the presence of cross-linking, polar groups, absorbed moisture and/or C=O [3, 72]. The presence of oxygen is identified by EDX [98, 99] and the presence of C=O has been detected by FTIR spectroscopy in PPDEA thin films [99]. The presence of absorbed moisture and/or C=O and polar group density probably increase with the increasing thickness of PPDEA thin films due to the presence of more dangling bonds and therefore increases the molecular mobility and hence increases the $\varepsilon'$ with increasing thickness.

![Graph](image)

**Fig. 4.44** Variation of $\varepsilon'$ of different thicknesses at room temperature of (a) as-deposited and (b) iodine doped as-deposited PPDEA thin films.
is a report on increase of $\varepsilon'$ due to increased molecular mobility available in plasma polymerized linalyl acetate thin films [126].

4.9.4 Temperature dependence of dielectric constant

Figs. 4.45 and 4.46 present the $\varepsilon'$ as a function of temperature of the as-deposited and iodine doped as-deposited PPDEA thin films respectively. The general trend of $\varepsilon'$ is to decrease with increasing temperature and this trend is also observed in all as-deposited and iodine doped as-deposited PPDEA thin films in the temperature range from 298 to 373 K. In the low-temperature range (298 to 373 K), a rapid decrease in $\varepsilon'$, followed by a slow decrease in the temperature range 373 to 398 K is observed for most of the samples. In low
frequency the temperature dependence of the $\varepsilon'$ reflects the temperature dependence of the $\varepsilon_0$. The lesser dependence of $\varepsilon'$ on temperature in the high frequency region and the higher dependence of $\varepsilon'$ on temperature in the low frequency region may be attributed to the thermal expansion of the polymer which causes the decrease of $\varepsilon'$ [33]. Vella and Toureille [127] have shown the loss of water molecules due to heating resulting in a decline in $\varepsilon'$ in this temperature range (298 to 373 K). In PPDEA thin films the exclusion of small amount of absorbed water in this temperature region is also detected in TG/DT analyses. This exclusion of absorbed water can decrease the $\varepsilon'$ in the temperature from 298 to 373 K.

Generally, the variation of $\varepsilon'$ with the temperature is related to the charge carrier which in most cases cannot orient themselves with respect to the direction of the applied field;

Fig.4.46  Variation of $\varepsilon'$ with temperature at different frequencies for iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
therefore, they possess a weak contribution to the polarization and hence to $\varepsilon'$. In PPDEA thin films, as the temperature increases, the bound charge carriers got enough thermal excitation energy to be able to respond to the change in the $\sigma_{ac}$ [128]. This $\sigma_{ac}$ change in turn decreased their contribution to the polarization leading to decrease of the $\varepsilon'$ due to high dielectric loss. The above observation suggests that PPDEA thin films are suitable for dielectric applications in the frequency regions of 0.1 to 100 kHz.

4.9.5 Variation of $\tan\delta$ with frequency and temperature

The $\tan\delta$ for PPDEA thin films of different thicknesses are calculated by the Eqn. 3.5. The variation of $\tan\delta$ with frequency and temperature are analyzed on as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses in the temperature range from 298 to 373 K and the plots of $\tan\delta$ vs. frequency are shown in Figs. 4.47 and 4.48 respectively. It is observed from the plots that in the low frequency region $\tan\delta$ decreases as the frequency increases followed by a loss minimum. This phenomenon is usually associated with ion drift, dipolar polarization or interfacial polarization involving ionic movement [41]. After that the $\tan\delta$ increases with the increase in frequency and attains a peak at around 100 kHz and then decreases. This phenomenon is also evident in the decrease of $\varepsilon'$, as the dipole orientation can not keep up at high frequency. In PPDEA thin films the relaxation might have occurred above 100 kHz ($1/\tau \geq 100$ kHz). This is indicating a fast polarization mechanism and generally labeled as the $\gamma$ process. The $\gamma$ process dominates the behavior of $\varepsilon'$ from 100 to $10^5$ Hz [60].

In the low frequency region $\tan\delta$ shows a loss minimum in the frequency range from 100-1000 Hz i.e. a low frequency relaxation process and the loss shifts toward higher frequency side with increasing temperature. In the higher frequency side there is a loss maxima observed at $f = 100$ kHz. Thus, it is observed that there are two types of relaxation processes present in the low and high frequency regions. The loss increase observed in the high frequencies is the low-frequency tail of the loss peak associated with $\gamma$ relaxation. The loss decrease in the range of 100 to 500 Hz is the high frequency tail of the loss peak associated with $\beta$ relaxation process. The high frequency tail of the low frequency relaxation may result owing to the slow motion of molecular groups in the PPDEA thin film structure i.e. may be due to $\beta$ relaxation process. The identical observations have been reported by Gonon et al. [33]. They characterized the low frequency (0.1 to 100 Hz) relaxation as $\beta$ process and that of high frequency (100 to 100 kHz) as $\gamma$ process of fluorocarbon thin films deposited by radio frequency sputtering of polytetrafluoroethylene.
They also ascribed about the β process (low frequency relaxation) in polymers due to the presence of C=O bonds, free ions, or defects. In PPDEA thin films the presence of C=O is detected in FTIR analyses and the presence of ions or free charges due to defects are also inferred in UV-vis analyses and DC electrical properties. These observations indicate β relaxation in the low frequency region. Thus it can be attributed that PPDEA thin films show two different relaxations i.e. β and γ processes in the lower and higher frequency regions respectively. The loss peaks are observed to shift towards the higher frequency side on increase in temperature. A shift of loss peak towards higher frequency side means reduction of the relaxation time. The increase in the maximum value of $\tan\delta$ with the

![Graphs showing variation of $\tan\delta$ with frequency measured at different temperatures for as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.](image)

Fig.4.47 Variation of $\tan\delta$ with frequency measured at different temperatures for as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
increase in temperature (from 373 to 398 K) and frequency indicates that the number of
close charge carriers increases by thermal activation [130]. But in the case of PPDEA thin films
the maximum value of $\tan\delta$ have not shown any definite trend in the lower temperature
region (298 to 373 K) which may be due to the evolution of small amount of absorbed
moisture in PPDEA thin films. In higher temperature region (373 to 398 K) the maximum
value of $\tan\delta$ increases with increasing temperature i.e. charge carriers increase by thermal
activation at higher temperature.

Fig.4.48  Variation of $\tan\delta$ with frequency measured at different temperatures for iodine doped as-
deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
In the case of amorphous polymers $f_{\text{max}}$ vs $1/T$ plots yields straight lines [90]. The relaxation time $\tau$ is determined from the frequency $f_{\text{max}}$ of $\tan\delta$ peak by the relation, $\tau = (1/2\pi f_{\text{max}})$. Fig. 4.49 shows the plot of $\ln \tau$ (relaxation time) against the reciprocal of absolute temperature for as-deposited and iodine doped as-deposited PPDEA thin films. Assuming the plots as a linear relation, the slope yields the energy for dielectric relaxation of 0.03 and 0.05 eV for as-deposited and iodine doped as-deposited PPDEA thin films respectively [131].

![Graph showing variation of $\ln \tau$ with reciprocal of absolute temperature for (a) as-deposited ($d = 200$ nm) and (b) iodine doped as-deposited PPDEA thin film ($d = 150$ nm).]
4.9.6 Comparison of AC electrical properties of as-deposited and iodine doped as-deposited PPDEA thin films.

The plots of $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$ against frequency of as-deposited and iodine doped as-deposited PPDEA thin films of different thicknesses at room temperature are shown in Figs 4.50, 4.51 and 4.52 respectively. It is observed that the $\varepsilon'$ values increase after iodine doping in as-deposited PPDEA thin films and this may be attributed to the presence of polarizable molecular iodine. The same explanation of the increase in $\varepsilon'$ of polymethyl methacrylate thin films after iodine doping is reported by Tanwar et al. [42]. The increase in $\varepsilon'$ and $\tan\delta$ due to iodine doping shows that an increased number of dipoles participating in the orientation process, while the frequency of orientation remains unchanged. The $\sigma_{ac}$ values also increase after iodine doping. The increase in $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$ can be explained due to the formation of charge transfer complex. The addition of iodine may also reduce the insulating capacity (by increasing $\sigma_{ac}$) due to introduction of localized states or sub levels. Tanwar et al. [42] reported that iodine may reside at various sights of polymer. It may undergo substitution into polymer chain at the amorphous or crystalline boundaries and preferentially into amorphous regions of the polymer. They asserted that addition of iodine creates additional hopping sites for the charge carriers and hence an increase in its concentration increases the $\sigma_{ac}$. In PPDEA thin films the addition of iodine enhances the polar character and thus making them electrically more conductive. Quamara et al. [41] stated that iodine generally diffuses preferentially in the less dense volume region of the polymer and is present either interstitially or trapped between the chain configurations and forms a charge transfer complex within the structure and helps in increasing the electron–hole pair concentration. As a result of the electrostatic interaction between the chain and iodine, the intermolecular interactions are reduced facilitating the motion of the molecules, eventually resulting in an increase in their mobility and the $\varepsilon'$. An increase in mobility also explains a higher dielectric loss in iodine-doped samples. The similar trend of $\varepsilon'$ and $\tan\delta$ are observed in the case of iodine doped as-deposited PPDEA thin films. This implies that PPDEA is capable to form the charge transfer complex in the presence of iodine. This charge transfer complex acts as excess carriers/electron-hole pairs in PPDEA. The formation of charge transfer complex is confirmed by a new absorption peak in the UV-vis spectra of iodine doped as-deposited PPDEA thin films.
Fig. 4.50 Dependence of $\sigma_{ac}$ on frequency measured at room temperature of as-deposited and iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
Fig. 4.51 Variation of $\varepsilon'$ with frequency measured at room temperature for as-deposited and iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
Fig. 4.52 Variation of $\varepsilon''$ with frequency measured at room temperature for as-deposited and iodine doped as-deposited PPDEA thin films of thicknesses: (a) 150 (b) 200 (c) 350 and (d) 450 nm.
4.10 Correlation Between Different Physical Properties of As-deposited and Modified PPDEA Thin Films

In EDX analyses the heat treated PPDEA thin films have shown a decrease in O and increase in C and the FTIR analyses have shown the extent of C=C which signifies the presence of conjugation. This conjugation due to heat treatment most probably increases the thermal stability and decrease the $E_g$ values. The FTIR analyses of iodine doped PPDEA thin films suggest modification of the bond length due to charge transfer complex formation which in turn decreases the $E_g$ and $\Delta E$, increases the thermal stability, $\sigma_{dc}$, $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$.

From the correlation in Table 4.15 it is depicted that for as-deposited PPDEA thin films the $E_{g(d)}$ values are found independent of thickness and $E_{g(i)}$ values increase with increasing thickness. The same trend is also observed for iodine doped as-deposited PPDEA thin films. The increasing trend of $E_{g(i)}$ can be correlated with the increasing trend of $\Delta E$ with increasing thickness at low temperature. The independence of $E_{g(d)}$ value on thickness can be correlated with the independent values of $\sigma_{dc}$ with thickness. But after iodine doping the $\sigma_{dc}$ values decrease with increasing thickness and the $E_{g(i)}$ values increase with increasing thickness. This means that the charge carriers participating in conduction process is varying with the thickness of PPDEA thin films. After iodine doping, the decreasing trend of $\sigma_{dc}$ with increasing thickness suggests that the thinner films absorb more iodine than the thicker films or the relative concentration of iodine is larger in thinner films than the thicker films.

The values of $\varepsilon'$ are found to increase with increasing thickness for both as-deposited and iodine doped as-deposited PPDEA thin films, may be due to the increased amount of radicals or dipoles with the increasing thickness. It is also observed that the values of $\varepsilon'$ increase in the case of iodine doped as-deposited PPDEA thin films in contrast to the as-deposited ones and this may be attributed to the presence of highly polarizable molecular iodine.

Table 4.15 Relation between optical and electrical (DC and AC) parameters.

<table>
<thead>
<tr>
<th>PPDEA Thin Films</th>
<th>Optical $E_{g(d)}$ $E_{g(i)}$</th>
<th>DC electrical $\sigma_{dc}$ (ohm-m) $^\dagger$ at 5 V (Ohmic region)</th>
<th>Low temperature $\Delta E$ (eV) at 5 V (Ohmic region)</th>
<th>AC electrical $\varepsilon'$ at 10 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>3.56 3.61 3.60</td>
<td>2.23 2.28 2.34</td>
<td>7.70 7.35 8.33</td>
<td>0.085 0.094 0.104</td>
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<tr>
<td></td>
<td>± 0.01 ± 0.01 ±</td>
<td>(eV)</td>
<td></td>
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</tr>
<tr>
<td>150 200 350</td>
<td>3.90 3.88 3.92</td>
<td>2.03 2.05 2.10</td>
<td>12.2 9.01 9.44</td>
<td>0.048 0.052 0.057</td>
</tr>
<tr>
<td>Iodine doped as-deposited</td>
<td>2.90 2.88 2.92</td>
<td>2.03 2.05 2.10</td>
<td>12.2 9.01 9.44</td>
<td>0.048 0.052 0.057</td>
</tr>
<tr>
<td></td>
<td>± 0.01 ± 0.01 ±</td>
<td>(eV)</td>
<td></td>
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</tbody>
</table>
5.1 Summary
From TG, DT and DTG analyses in air environment, the as-deposited PPDEA is found thermally stable up to about 580 K. The thermal stability is increased to about 626 K after heat treatment. Iodine doping does not change the thermal stability significantly. From DT, TG and DTG analyses in N\textsubscript{2} environment, the as-deposited PPDEA is found to be thermally stable up to about 500 K. Comparing the DT, TG and DTG traces of as-deposited PPDEA in air and N\textsubscript{2} environments, it is observed that the weight loss and the thermal stability temperature is less in N\textsubscript{2} environment than that in air due to the oxidation in air environment. The DSC analyses show T\textsubscript{g} points at about 275 and 290 K for as-deposited and heat treated PPDEA respectively. The $\Delta C_p$ for T\textsubscript{g} is calculated out to be about 121.8 J/kg-K and 357 J/kg-K for as-deposited and heat treated PPDEA respectively. In both as-deposited and heat treated PPDEA there is a broad endothermic peak after T\textsubscript{g} point which may involve ice melting and evolution phenomenon of the small amount of absorbed water inherent in PPDEA.

The surface morphology of as-deposited and heat treated PPDEA thin films are found uniform and pinhole free. The iodine doped as-deposited PPDEA has become comparatively smoother than that of the as-deposited ones. The cross-section image has proved the smoothness of PPDEA thin film.

The Wt % reduction of N and O and increase of C in heat treated PPDEA compared to those of as-deposited PPDEA thin films correspond to some chemical changes during heat treatment. The iodine doped as-deposited PPDEA thin film contains C, N, O and iodine in it. The decrease in Wt % of C, the increase in Wt % of O and the presence of iodine imply possible formation of charge transfer complex in iodine doped as-deposited PPDEA thin film.

The FTIR absorption peaks for PPDEA thin films are not sharp as compared to DEA monomer but most of the FTIR absorption features of DEA are observed in the PPDEA spectrum with a little shift in wavenumbers and the intensity of the absorption bands decrease, due to superposition of some bands with the wide absorption bands. The formation of wide bands due to merging of small bands indicates structural rearrangement. This means that the plasma polymerization technique affects the chemical structure of DEA during PPDEA thin film formation. The C=C of benzenoid and quinoid ring structure and methyl and methylene bands of ethyl group of the starting monomer are retained after polymerization i.e. PPDEA contains an aromatic ring structure with C-N and ethyl side groups. In FTIR analyses the shift of most of the absorption peaks of heat treated PPDEA to
different wavenumbers and the decrease in intensity of the absorption bands compared to as-deposited PPDEA may correspond to the structural rearrangement due to heat treatment. The reduction of C-H and C-N bands in heat treated PPDEA signifies the occurrence of H and N loss. The loss of H and N may allow the presence of C=C bands as a result of crosslinking between different C atoms due to heat treatment. The formation of C=O in as-deposited and heat treated PPDEA suggests that some of the C atoms are in an oxidized state. The iodine doped as-deposited PPDEA has peaks that are mostly similar to those of the as-deposited PPDEA with a few deviations. It can be seen from the spectrum of iodine doped as-deposited PPDEA that there are little increase and/or decrease in the band intensity and shift in few absorption bands compared to the as-deposited ones. These changes occur because iodine possibly have modified the bond length and facilitates shifting of some bands corresponding to some functional groups along the wavelength axis.

The value of $E_{g(d)}$ for as-deposited PPDEA thin films of different thicknesses are almost constant, which is about 3.60 eV and $E_{g(i)}$ values slightly increase from 2.23 to 2.38 eV with increasing thickness (100-350 nm), due to the increase in fragmentation/cross-linking with plasma duration. It is observed that the $E_g$ values of PPDEA thin films lies in the range of $E_g$ values of different plasma polymerized thin films and some what larger than that of the other plasma polymerized aniline/aniline derivatives due to the ethyl group substituted benzene ring in the precursor. The values of $E_u$ of PPDEA thin film decrease from 0.60 to 0.47 eV and the $\sigma_s$ values change from 0.043 to 0.055 as the film thickness increases. The slight increase in $E_{g(i)}$ and the decrease in $E_u$ with increasing film thickness possibly be due to some reduction of localized electronic states in the $E_g$. The $\sigma_s$ values suggest that the absorption edge changes with increasing film thickness.

The $E_{g(d)}$ and $E_{g(i)}$ values are observed to be 3.51 to 2.73 eV and 1.26 to 2.25 eV respectively for heat treated PPDEA thin films of different thicknesses. For aged PPDEA thin films the $E_{g(d)}$ and $E_{g(i)}$ values are observed to be 3.55 to 3.51 eV and 2.12 to 2.25 eV respectively. The variation in $E_g$ values reveals that the band gap decreases considerably due to heat treatment and also decreases with the heat treatment temperature. Aging have not caused any appreciable change in $E_g$ values. Consequently, the other optical parameters ($E_u$, $\sigma_s$ and $K$) for heat treated and aged PPDEA thin films are also changed.

It is observed that, after iodine doping into the as-deposited PPDEA thin films, each UV-vis absorption spectrum of different thicknesses show new shoulder/peak in the higher wavelength side at about 360 nm and the peak at 300 nm of as-deposited PPDEA thin film slightly shifted to the higher wavelength side at about 305 nm. This type of spectral change
is due to the formation of charge transfer complex resulting from the reaction of acceptor type iodine and donor type PPDEA. The $E_{g(d)}$ value is found to be about 2.95 eV and the $E_{g(i)}$ values are varied from 2.05 to 2.13 eV for different thicknesses. It is observed that iodine doping effects/decreased the $E_{g(d)}$ of as-deposited PPDEA thin films more than that of the $E_{g(i)}$. The less change in $E_{g(i)}$ may occur because the localized states are not affected much on iodine doping. The $E_a$ values decrease from 0.36 to 0.30 eV and $\sigma_s$ values increase from 0.070 to 0.086. Thus it can be attributed that a charge transfer complex resulting from iodine doping initiates a change in the optical parameters of PPDEA thin films. It is found that the $E_{g(i)}$ and $E_{g(d)}$ values decrease from 2.15 to 2.05 eV and 2.92 to 2.86 eV respectively for the doping period ranging from 15 to 60 min for PPDEA thin film of 150 nm thick. The decreasing trend of $E_{g(d)}$ with increasing doping period indicates that $E_g$ values of PPDEA thin films can be decreased/changed by varying the iodine doping period via formation of charge transfer complex. The decrease of $E_a$ values with increasing doping period can be attributed to the reduction of defect states with increasing iodine doping period and therefore increasing the structural ordering which is responsible for the decrease in $E_{g(i)}$ values of iodine doped PPDEA thin films with increasing doping period.

From DC electrical properties it is observed that iodine doping affects the electrical transport properties of PPDEA substantially. The formation of charge transfer complex and an increase in electrical conductivity are explained on the basis of the interaction between donor type PPDEA and acceptor type iodine. Iodine might have formed excess charge carrier (free electrons or holes) which governed the generation of PF type conduction process (bulk limited) in iodine doped as-deposited PPDEA thin films of different thicknesses rather than Schottky (electrode limited) which is dominant in those of as-deposited PPDEA. The $\varphi_{SBH}$ of as-deposited PPDEA thin films, of different thicknesses, ranging from 0.36 to 0.5 eV which is weakly dependent on film thickness. For as-deposited PPDEA thin films, lower temperature $\Delta E$ is found to be about 0.093 ± 0.013 eV and 0.081 ± 0.002 eV and that at the higher temperature region is 0.91 ± 0.12 eV and 0.90 ± 0.05 eV for applied voltage of 5V (Ohmic) and 15 V (non-Ohmic) respectively. For iodine doped as-deposited PPDEA thin films the lower temperature $\Delta E$ is found to be about 0.055 ± 0.005 and 0.068 ± 0.0075 eV and those for high temperature is found to be about 0.80 ± 0.10 and 0.75 ± 0.04 eV for 5 and 15 V respectively. The values of $\Delta E$ and their changes from lower to higher values with the increase in temperature in as-deposited and iodine doped as-deposited PPDEA thin films may be attributed to a transition from a hopping regime to a regime dominated by distinct energy levels. The $\Delta E$ of as-deposited PPDEA thin films are
higher compared to those of the iodine doped as-deposited ones. The lower value of $\Delta E$ in iodine doped as-deposited PPDEA thin films is possibly due to the carrier formation. The formed charge carriers ensues the lower energy to activate the carriers to conduct through the PPDEA thin films.

It is found that $\sigma_{ac}$ of as-deposited and iodine doped as-deposited PPDEA thin films increases as frequency increases for all the temperatures scanned. The calculated values of the frequency exponent, $n$ of as-deposited and iodine doped as-deposited PPDEA thin films correspond Debye-type relaxation process in the lower frequency region and other than Debye type relaxation process in the high frequency region. The temperature dependence of $\sigma_{ac}$ in as-deposited and iodine doped as-deposited PPDEA thin films in the low frequency region suggest that the conduction may be dominated by hopping of carrier between the localized states at all temperatures. It is observed that $\varepsilon'$ decreases slowly with increasing frequency for as-deposited and iodine doped as-deposited PPDEA thin films at fixed five different temperatures which indicates space charge or interfacial polarization at low frequency and dipolar polarization at higher frequency region. The weak dependence of $\varepsilon'$ on temperature in the high frequency region and the strong dependence of $\varepsilon'$ on temperature in the low frequency region may be attributed to the thermal expansion of the PPDEA thin films which causes the decrease of $\varepsilon'$. At the higher temperature region (373-398 K) the maximum value of $\tan\delta$ increases with increasing temperature i.e. charge carriers increase by thermal activation at higher temperature. The energy for dielectric relaxation is found to be 0.03 and 0.05 eV for as-deposited and iodine doped as-deposited PPDEA thin films respectively. The increased values of $\varepsilon'$ are observed in the case of iodine doped as-deposited PPDEA thin films and this possibly be attributed to the presence of highly polarizable molecular iodine. The increase in $\varepsilon'$ and $\tan\delta$ due to iodine doping suggest that an increased number of dipoles participating in the orientation process, while the frequency of orientation remains unchanged. The $\sigma_{ac}$ values also increase after iodine doping. The increase in $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$ can be explained due to the formation of charge transfer complexes.
5.2 Conclusions

The as-deposited PPDEA is found thermally stable upto about 580 K which increased due to heat treatment and is not changed significantly due to iodine doping. The weight loss and the thermal stability are decreased in N\textsubscript{2} environment than that in air. The as-deposited and heat treated PPDEA have shown T\textsubscript{g} of about 275 and 290 K with the ΔC\textsubscript{p} of T\textsubscript{g} of about 121.8 J/kg-K and 357 J/kg-K respectively. In heat treated PPDEA the Wt% reduction of N and O and increase of C than that of as-deposited ones corresponds to some chemical changes during heat treatment. The Wt % decrease of C, increase of O and the presence of iodine imply the possible formation of charge transfer complex in iodine doped as-deposited PPDEA thin film. The FTIR absorption peaks of PPDEA revel that C=C of benzenoid and quinoid ring structure and methyl and methylene bands of ethyl group of the DEA monomer are retained even after plasma polymerization. The FTIR spectra of heat treated PPDEA correspond to the structural rearrangement due to heat treatment. The occurrence of hydrogen and N loss depicted by the reduction of C-H and C-N bands in heat treated PPDEA may allow the presence of C=C bonds as a result of cross-linking between different C atoms. The increase and/or decrease and shifting of few absorption bands of iodine doped as-deposited PPDEA compared to the as-deposited PPDEA correspond to the modifications of the bond length. The E\textsubscript{g} is decreased considerably due to heat treatment and not changed appreciably due to aging. Consequently, the other optical parameters (E\textsubscript{u}, \sigma\textsubscript{s} and K) also changed. Both of the E\textsubscript{g(d)} E\textsubscript{g(i)} values are found to decrease significantly with increasing iodine doping period. The increase of \sigma\textsubscript{dc} and decrease of ΔE of iodine doped as-deposited PDEA thin films than those of as-deposited ones are explained on the basis of the formation of charge transfer complex due to the interaction between donor type PPDEA and acceptor type iodine. Iodine might have formed excess charge carrier (free electron or holes) which regulated the generation of PF type conduction process in iodine doped PPDEA thin films of different thicknesses rather than Schottky, dominating in as-deposited PPDEA thin films.

The change in ΔE from lower to higher values with the increase in temperature in both (as-deposited and iodine doped as-deposited) of the PPDEA thin films may be attributed to a transition from a hopping regime to a regime dominated by distinct energy levels. The σ\textsubscript{ac} of both of the PPDEA thin films increase as the frequency increase for all the measurement temperatures. Both of the PPDEA thin films corresponds Debye-type and other than Debye type relaxation process in the lower and high frequency regions respectively. In the low frequency region the temperature dependence of σ\textsubscript{ac} in both of the PPDEA thin films suggest hopping type conduction of carrier between the localized states at all temperatures.
The frequency dependence of $\varepsilon'$ can be attributed to the interfacial and dipolar polarization in the low and high frequency regions respectively for both of the PPDEA thin films at fixed five different temperatures. At higher temperature region (373-398 K) the maximum value of $\tan\delta$ increases with increasing temperature i.e. charge carriers increase by thermal activation at higher temperature. After iodine doping, the increase in $\sigma_{ac}$, $\varepsilon'$ and $\tan\delta$ can be explained due to the formation of charge transfer complexes or the presence of highly polarizable molecular iodine.

Thus, it can be concluded that thermal, structural and optical properties of PPDEA thin films were changed significantly due to heat treatment and iodine doping and were not changed appreciably due to ageing compared to those of the as-deposited ones. Iodine doping increased the $\sigma_{dc}$, $\sigma_{ac}$, and $\varepsilon'$. The findings of the physical properties of as-deposited and modified PPDEA thin films suggest that PPDEA thin films may find application in electronic, optoelectronic devices, thin film dielectrics, etc.
5.3 Suggestions for further study

All the characterizations done in the present study represents thermal, morphological, structural, optical and electrical (DC and AC) properties of as deposited, heat treated, aged and iodine doped as-deposited PPDEA thin films. Beyond these characterizations some other can be done to establish the suitable application areas for PPDEA thin films. Some of them are stated below-

The chemical investigation can be done by EA or time-of-flight secondary ion mass spectroscopy (TOF-SIMS). The atomic force microscopy (AFM) can be used to see the smoothness of the surface. The XPS investigation should be carried out in order to see the bonding of different functionalities in the PPDEA thin films. It also can provide quantitative information of the functional groups present. The XRD analysis could be performed to see the extent of crystalline and amorphous phases.

The electron spin resonance (ESR) study may be carried out to see the nature and source of radicals in this material. For studying the charge storage and charge relaxation the thermally stimulated depolarization current (TSDC) can be measured.

The surface energy of PPDEA can be determined by contact angle (CA) measurement. It can be also deposited as a coating on other polymers. The microhardness analysis can be done to see the level of hardness of PPDEA thin films.

The electrical (DC and AC) measurement can be carried out on heat treated and aged PPDEA thin films. The heat treatment of electrical samples is not done because, the Al electrodes become oxidized due to heat treatment. For electrical measurement the doping of iodine by varying the doping period were also tried but the Al electrode start to degrade for longer doping period.

The electrical properties of PPDEA thin films also can be investigated in an asymmetric electrode configuration.

In the present study iodine doping is carried out by exposing the PPDEA thin films in iodine crystals but the doping of these films also can be carried out simultaneously with the monomer gas (in situ doping) while preparing those films in the plasma chamber.

The PPDEA can be prepared by varying the plasma process parameters and also can be prepared by an inductively coupled, plasma polymerization set-up with RF power and their different physical properties can be investigated.
Chapter 5

Conclusions

References


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[64] Thomas, Os, M. V., ‘Surface modification by plasma polymerization: film deposition,


APPENDIX 1:
Publications and Presentations Based on This Work

Publications:

Paper Presentation in Conferences