Polymer thin films display anisotropy under the influence of an electric field. Generally they are said to be displaying ordinary optical properties when the electric field is perpendicular to the c-axis and exhibit extra ordinary optical properties when the electric field is parallel to the c-axis. The anisotropy is a strong function of the crystallographic and textural orientations. If the polymer chains are aligned/oriented along the same direction, the anisotropy of the polymeric material would be similar to that of a single crystal. If the chains have the same probability of occurrence for all textures and orientation, the optical properties of the material would be isotropic. The effective dielectric function of a polymeric material can be evaluated as a tensorial average assuming that the medium is composed of uniaxial crystals, oriented in random directions. The spectroscopic ellipsometry (SE) is an excellent and handy tool for the characterization of thin films. The surface roughness, thickness, optical constants and the pseudo dielectric parameters, can be evaluated from the ellipsometric measurements. These experiments provide a wealth of information about the material under investigation.

The optical constants and dielectric functions of rf plasma polymerized polyaniline thin films in their pristine and iodine doped films were estimated by spectroscopic ellipsometry for different angles of incidence $55^0$, $60^0$ and $65^0$, in the energy regime $0.75$ eV to $4.6$ eV. The optical constants $n$, $k$, $e_1$, $e_2$ and energy band gaps for different angles of incidence were evaluated. Polyaniline (PANI) was doped with iodine ($insitu$) and the effect of iodine doping on the optical properties these films was also carried out using spectroscopic ellipsometric studies. Both pristine and iodine doped PANI exhibited low-$k$
properties in the low frequency regime (100 Hz - 2 MHz)\textsuperscript{1,2}. So both pure and doped polyaniline films were subjected to the ellipsometric studies with a new objective of verifying their low-k behaviour at optical frequencies. By a simple calculation and employing the optical constant values at these frequencies, the optical conductivity of these pristine and iodine doped films were determined. It was found that there exists an insulator to metal transition at optical frequencies.

This chapter describes the evaluation of the optical constants \( \text{viz.} \, n, k \) and the pseudo dielectric constants of both the pristine and iodine doped plasma polymerised polyaniline thin films in the energy regime 0.725 eV to 4.6 eV. This is carried out by employing a J.A.Woollan Variable Angle spectroscopic ellipsometer (VASE) with multiple angles of incidence 55, 60 and 65 degrees\textsuperscript{3,4}. Finally Bruggman effective medium\textsuperscript{3} model was applied to fit the data and it was found that the pseudo dielectric function of the randomly oriented polycrystalline material resembles that of a single crystalline material. Surface roughness and optical smoothness of these films were also found out and were compared with the results obtained from the AFM and from the Dektac 6M Stylus profiler.

### 7.1 Ellipsometry measurements

In the ellipsometry measurement, the polarizer was tracked with the measured ellipsometric angle ‘\( \Psi \)’. Measurements at negative and positive polarization angles were averaged and an automatic retarder allowed the accurate determination of the difference in phase \( \Delta \) over the whole range of 0-360\textdegree{} and of partial depolarization. All the measurements were performed at room temperature. From the ellipsometric angles \( \Psi \) and \( \Delta \), the ratio of the diagonal reflection Jonnes matrices elements \( \frac{r_{pp}}{r_{ss}} = \tan \Psi \exp \Delta \) can be calculated. Here \( r_{pp} \) and \( r_{ss} \) are the complex Fresnel reflection coefficients parallel and perpendicular to the plane of incidence. Extraction of useful information from the ellipsometric data begins with the construction of an optical model for the polymer thin film on glass substrate. The experimental setup is described in detail in chapter 3.
7.2 Optical modeling for ellipsometry measurements

Extraction of useful information from the ellipsometric data and its interpretation begins with the construction of an appropriate optical model for the polymer film on the glass substrate. The model taken into account must consist of surface roughness layer, polymer film and glass substrate. The surface roughness layer in the optical model for the polymer film was analysed with an Effective Medium Approximation (EMA). The thickness of the polymer film was obtained by fitting the data in the highly transparent region of the spectrum using Cauchy dispersion relation. The results for n and k in the transparent region obtained from the Cauchy dispersion relation by performing a point-by-point fit starting from the transparent region to extract approximate values of the optical functions. A brief theory about these aspects is already provided in chapter 3.

7.3 Measurements of film thickness and surface roughness

The thickness of pristine plasma polymerised polyaniline was estimated and found to be 745.9 ± 0.6nm. The surface roughness was evaluated and was 1.8 nm with a mean square error (MSE) of 6.79 Å. It is known that the Bruggeman Effective Medium approximation (BEMA)\textsuperscript{6}, provides the overall time evolution of the spectroscopic ellipsometry (SE) and is an accepted method for the analysis of the SE data for bulk as well as the thin film having microscopic rough surfaces and interfaces, and with out further characterization, the surface roughness and film thickness obtained are assumed to be believable. This value of surface roughness obtained in the case of plasma polymerised polyaniline match very well with that of the rms value of surface roughness measured by Guifang Li \textit{et al} for PMMA films and estimated from the atomic force microscopy (AFM) and stylus probe\textsuperscript{7}. Here the very low surface roughness value exhibited by these films is important and assume significance from an application point of view. The low surface roughness of plasma polymerised polyaniline (PPANI) could be attributed to the following. The PPANI surface consists of small hills and valleys. The sticking coefficient of valley is slightly
greater than that of the hills and there occurs significant lateral diffusions and surface migration of the adsorbed species on the surface. This confirms that the technique of plasma polymerization can be employed to produce extremely smooth films with very small surface roughness when compared to films prepared by other conventional techniques.

![AFM photograph of plasma polymerised aniline thin films-Pristine](image)

**Figure 7.1.a:** AFM photographs of RF plasma polymerised aniline thin films—Pristine

The surface roughness and the thickness of the plasma polymerised thin films obtained from the ellipsometric technique match very well with the values obtained from the measurements carried out by the stylus probe and AFM. Figure 7.1 shows the AFM picture of the pristine and iodine doped RF plasma polymerised thin film. Stylus probe analysis also showed the surface roughness of RF plasma polymerised polyaniline thin films 20 Å. For the iodine doped film, the film thickness is 2354.2 Å and the surface roughness is 17 Å.
**Spectroscopic Ellipsometric Characterisation …**

Figure 7.1.b: AFM photographs of RF plasma polymerised aniline thin films in the iodine doped form

The ellipsometric angle ‘Ψ’ vs photon energy graph for the pristine and iodine doped films are depicted in figure 7.2 and figure 7.3 respectively.

Figure 7.2: SE Experimental spectra of ellipsometric angles Ψ for the plasma polymerized films of poly aniline (PANI) as acquired at various angles of incidence. The model fit is also shown.
Chapter 7

It can be seen that the variation of $\Psi$ with energy is oscillatory in nature. There is marked difference in the behaviour for the pure and doped samples. This data provides information at different depths of the samples. At lower photon energies, the penetration depth can be longer than the film thickness and this leads to interference fringes. This can be clearly seen from figure 7.2. and figure 7.3. The experimental data were successfully fitted and this fit almost coincides with that of the experimentally observed data. At higher photon energies, the penetration depth decreases and the film become opaque.

![Generated and Experimental](image)

**Figure 7.3:** SE Experimental spectra of ellipsometric angles $\Psi$ for the plasma polymerized films of poly aniline iodine doped (PANI) as acquired at various angles of incidence. The model fit is also shown.
Figure 7.4: SE Experimental spectra of ellipsometric angles and $\Delta$ for the plasma polymerized films of poly aniline (PANI) as acquired at various angles of incidence. The model fit is also shown.

Figure 7.5: SE Experimental spectra of ellipsometric angles and $\Delta$ for the plasma polymerized films of poly aniline doped (PANI) at various angles of incidence. The model fit is also shown.
Chapter 7

7.4 Pseudo dielectric functions and critical point transitions

The pseudo dielectric constants viz. $\varepsilon_1$ and $\varepsilon_2$ for the pristine and iodine doped plasma polymerised thin film samples are evaluated from the SE measurements. They are plotted separately and are shown in figure 7.6, 7.7, 7.8 and 7.9. From a study conducted in our lab\(^2\), it was found that these films exhibited low-k behaviour at lower frequencies (100 Hz to 2 MHz). It was our endeavor, in this study, to verify the same findings at higher frequencies especially in the optical regime. It has been found that at optical frequencies also, the same behaviour is observed, both in the case of pristine and iodine doped plasma polymerised polyaniline.

![Generated and Experimental](image)

**Figure 7.6:** Pseudo dielectric constant (real) of plasma polymerised polyaniline sample in its pristine form. For different values of the angle of incidence. The model fit is also shown.
Spectroscopic Ellipsometric Characterisation …

Figure 7.7: Pseudo dielectric constant (real) of plasma polymerised polyaniline sample in its iodine doped form. For different values of the angle of incidence. The model fit is also shown.

Figure 7.8: Pseudo dielectric constant (imaginary) of plasma polymerised polyaniline sample in its pristine form for different values of the angle of incidence. The model fit is also shown.
Chapter 7

Figure 7.9: Pseudo dielectric constant (imaginary) of plasma polymerised polyaniline sample in its iodine doped form for different values of the angle of incidence. The model fit is also shown.

The pseudo dielectric functions of the films were calculated using the Bruggman Effective Model. The static dielectric constant is a limit of $E \to 0$ of the complex dielectric constant given by $\varepsilon = \varepsilon_1 - i\varepsilon_2$ the real $\varepsilon_1$ and imaginary $\varepsilon_2$ of the dielectric function are related by Kramers-Kronig relation and is as follows.

\[
\varepsilon_1 = \varepsilon_0 + \frac{2}{\pi} \text{P} \int \frac{E'\varepsilon_2(E')}{E'^2 - \varepsilon_0^2} dE'.
\]

Here P denotes the principal value of the integral. From this equation, it is clear that the dielectric function $\varepsilon_1$ of the dielectric material originates from the absorption over the entire spectral range, which includes electronic, ionic and dipolar absorptions corresponding to the ultraviolet, infrared and microwave regions\textsuperscript{10,11}. The electronic contribution of the dielectric constant originates from the inter band electronic transitions and gives rise to a refractive index dispersion in the visible region. The ionic contribution corresponds to the molecular vibration. Here in this case, the ionic contributions are disregarded since it is important only in polar liquids and gases but negligible for solids. The
SE measurement was recorded in the entire spectral range which covers ultraviolet, visible and near infrared regime. The measurements were taken for three angles of incidence $\nu = 55^\circ, 60^\circ$ and $65^\circ$. The measured data was fitted to the model dielectric function and the values of $\varepsilon_1$ and $\varepsilon_2$ are plotted against the photon energies. The behaviour is found to be oscillatory in nature. The dependence of the real and imaginary parts of the dielectric constant with photon energy reveals an anisotropic behavior for the plasma polymerized films and this anisotropy is reflected in its refractive index and absorption coefficient$^{12,13}$. The averaged value of pseudo dielectric functions (real) of the films is given in figure 7.10 and 7.11 respectively.

Figure 7.10 depicts the variation of the real part of the dielectric constant with photon energy (in log scale) for pristine and iodine doped RF-PPANI films.

![Figure 7.10: The averaged value of pseudo dielectric functions (real) of the rf PANI films](image)

At lower photon energies the dielectric constant of the pure plasma polymerised polyaniline thin film is smaller when compared to that of the doped film up to a photon energy value of 3.8 eV. In the low energy regime up to 1.4
eV, the dielectric constant of the doped and pure films increases almost exponentially with the photon energy and from that energy onwards the dielectric constant value of the doped thin film decreases with increase in frequency. The dielectric constant of the pristine thin film increases and attains a maximum value at 2.8 eV and then decreases. At photon energy corresponding to 3.8 eV the value of the dielectric constant of pristine films becomes higher than that of the dielectric permittivity of the iodine doped samples. Beyond a photon energy corresponding to 3.8 eV the permittivity value of the iodine doped samples decreases sharply. This is because at IR frequencies the dominant contributing factor to keeping the low dielectric values is ionic polarization. In the case of doped samples, doping induces charged defects and contributes to the polarization caused by the ionic polarization\textsuperscript{14}. This might increase the dielectric constant of doped samples in this energy regime. In the case of iodine doped films the relaxation of polarization occurs at energy of 1.4 eV. In the visible region the electronic polarization is dominant over the ionic polarization and as a result, the dielectric constant of the pristine samples increases while that of the doped samples decreases.

![Figure 7.11](image.png)

**Figure 7.11:** The averaged value of the imaginary part of dielectric constants for pristine and iodine doped films.
**Spectroscopic Ellipsometric Characterisation** …

At higher values of photon energy the electronic polarization of the pristine films persists. The dielectric constant of the doped film decreases since in the doped films, since the ionized defect states contribute towards the conductivity of the samples at higher energy regime and the dielectric constant of the doped samples decreases. The average value of the imaginary part of dielectric constant is evaluated and depicted in figure 7.11

### 7.5 Evaluation of optical constants

The dielectric constant can also be considered as the manifestation of different interband transitions resulting from the applied electric field. The imaginary parts of the dielectric response is related to the combined density of states(DOS) $\mu$, given in equation 7.2. The function $\delta$ represents the spatially joined DOS between valance $\mathbf{k}_{v}$ and conduction $\mathbf{k}_{c}$ band states differing by energy $E = h\omega$ of the incident light. The imaginary part of the dielectric constant can be obtained from the equation 15

$$
E_{2} = \frac{4E^{2}h^{2}}{\pi\mu^{2}E^{2}} \int dk |P_{v} \mathbf{k}_{v}\mathbf{k}_{c}|^{2} \delta \mathbf{k}_{c} \mathbf{k}_{v} E_{v} E_{c} E^{2}
$$

Here $|P_{v} \mathbf{k}_{v}|^{2}$ is the momentum matrix elements between the valance and conduction band states and the integration is performed over the first Brillouin zone(BZ). Critical points (CPs) in the second derivative of the spectrum correspond to the energy at which the joint DOS shows strong variations. The variations of DOS are a function of energy. It may be noted here that the critical point energies correspond to the fundamental $E_{1}$ and the second transition $E_{2}$ corresponds to the $\pi \rightarrow \pi^*$ transition in both pristine and iodine doped films.
Figure 7.12: Second derivative of Epsilon2 of pristine PANI thin film. Minimum corresponds to the critical point energies. The figure shows two optical transitions—the fundamental optical bandgap at 3.185eV and second transition at 4.178eV.

Figure 7.13: Second derivative of Epsilon2 of iodine doped sample. Minimum corresponds to the critical point energies. The figure shows three optical transitions; the fundamental optical bandgap at 1.66eV, second transition at 2.396eV and the third at 2.825eV.
7.6 Optical constants and optical anisotropy studies on plasma polymerised aniline thin films

The spectral dependence of the complex refractive index \( n = n_1 + in_2 \) and the investigations on the dependence of the fundamental \( \pi \rightarrow \pi^* \) optical transition on a polymer backbone of thin conjugated polymer thin films are of
fundamental interest. This is also important from an application point of view. The internal quantum efficiency of a polymeric LED is related to the factor $1/\Phi n^2$ where $n$ is the real part of the refractive index of the polymeric film. The optical anisotropy strongly affects the quantum efficiency. This is because the refractive index $n$ of the polymer is employed to evaluate the angular range of escaping light and the quantum efficiency depends on the incident angle of the light beam to the surface normal$^{16,17}$. The ellipsometric angles $\Psi$ and $\Delta$ at different angles of incidence reflects the anisotropic behavior of the film$^{16,19}$. The phase relation of $n$ and $k$ with each other shown in figure 7.12 and 7.13 are an indication of optical anisotropy which leads to a possible non linear optical behavior of the films.

It must be mentioned here that the deposition parameters during plasma polymerisation greatly influences the dielectric behaviour of the polymer thin films. RF power, current density, vapour pressure, and monomer flow rate has a profound influence on the dielectric and optical properties of these films.

### 7.7 Optical conductivity measurements of plasma polymerised aniline thin films

The optical conductivity of the films is estimated by employing the Drude model which describes the contribution to the classical dielectric function. The dependence of $\varepsilon$ with $\omega$ can be written as$^{20}$

$$\varepsilon \approx \varepsilon_i(\omega) + i \left( \frac{4\pi}{\omega} \right) \sigma$$  \hspace{1cm} (7.3)

This model has been successful in describing the electronic properties of simple metals. However when the disorder is introduced with the magnitude of disorder potential it is comparable to the band width and multiple scattering causes the electronic state near the Fermi energy ($E_F$) to become localized. In such a system, disorder induced localization causes transition from metal to insulator. As a result the charge dynamics of a disordered system become fundamentally different from that of metals$^{21}$. 


Spectroscopic Ellipsometric Characterisation …

The electronic states of conducting polymers are strongly degenerate on the amount of disorder. Although heavily doped conducting polymers have a metallic density of states at the Fermi Energy $E_F$, their transport properties are dominated by the disorder which originates from a combination of partial crystallinity (molecular scale disorder) and inhomogeneous doping$^{22,23}$.

The complex optical conductivity $\sigma = \sigma_1 + i\sigma_2$ is related to the real and imaginary parts of the dielectric constant as $\sigma_1 = \frac{\varepsilon_2 \omega}{4\pi}$ and $\sigma_2 = -\frac{\varepsilon_1 - 1}{4\pi} \frac{\omega}{\nu}$ with angular velocity $\omega = 2\pi\nu$ and $\nu = c/\lambda$ in cm$^{-1}$.

Figure 7.16: The real part of the optical conductivity of the thin films. The inset shows the log (real part of the optical conductivcity) vs. Photon energy in log scale.

The optical conductivity of the thin films is extremely small up to photon energy of 2.3 eV for pristine and 1.29 eV in the case of doped films respectively and then the optical conductivity increases. It is to be noted here that, a transition
occurs from insulator to metal in both pristine and doped samples in the optical frequency regime.

![Imaginary part of the optical conductivity](image)

*Figure 7.15* Imaginary parts of the optical conductivity

The enhancement of optical conductivity in doped and pristine samples correspond to the energy gaps of the pristine and iodine doped samples are calculated using Karammers- Kroning model.
Conclusion

By employing spectroscopic ellipsometric studies, the optical and the dielectric parameters of plasma polymerised thin films of polyaniline in its pristine and iodine doped forms are evaluated. It is found that the low dielectric constant (low-k) values exhibited by the thinfilms at lower frequencies are found to be existing in optical frequencies too. From optical conductivity calculations it is found that the optical conductivity attains metallic nature at high frequencies. These studies all points to the fact that plasma polymerised thin films are structurally anisotropic.
Chapter 7

References