DETERMINATION OF OPTICAL CONSTANTS OF A CONDUCTING POLYMER USING REFLECTION ELLIPSOMETRY TECHNIQUE

By

GEBREGIORGIS ABRAHA

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Dedicated To my parents.

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Abstract

The reflection Ellipsometry technique is employed for the determination of optical constants of a conducting polymers of thin films using a He-Ne laser wavelength of 632.8 nm and tunable diode laser wavelength 808.4 nm, respectively. The same technique is also applied to determine the thickness of the thin film. In this experiment two methods are employed to determine the refractive index of the sample. The rotating analyzer ellipsometry technique and the static photometric technique. The refractive indices obtained for the polymer sample at the rotating analyzer angle of incidence 60^0 using He-Ne laser of wavelength 632.8 nm and tunable diode laser of wavelength 808.4 nm are 1.73320 ± 0.000013 and 1.73010 ± 0.000015, respectively. Almost all the results are reproduced using, the second method called static photometric technique. The average calculated results at the wavelengths of 632.8 nm and 808.4 nm are 1.7577 and 1.5862,respectively.

The results for the thickness measurement obtained using Ellipsometry technique strongly agrees with the results obtained from the talystep measurement, the thickness of the sample lies between $30 - 40$ nm, where as the calculated results at wavelengths of 632.8 nm and 808.4 are 37.8 ± 0.00098 nm and 37.5 ± 0.00077 nm, respectively.

Introduction

Conjugated polymers are attractive materials for use as the active semiconductor in large area, low-cost electronic devices. Polymer Light Emitting Diodes (LEDs) are already finding commercial applications in Displays, and the performance of Polymer-based Photovoltaic devices is improving rapidly [2, 3]. Both of these types of devices involve multilayered structures incorporating electrode materials and polymer layers with thickness comparable with wavelength of optical radiation. Electrical characterization of the devices and above all, their optical properties of polymer plays a great role on the functions and efficiency of devices, since the optical properties of polymers are not yet well established, and requires further investigation. So optical characterization is necessary to make conjugated polymers in use in the application areas. There were some efforts made on optical characterization [2, 3, 4]. Although there are different methods for determination of optical constants for conjugated polymer films, such as transmission ellipsometry, diffraction ellipsometry here we use reflection ellipsometry in this thesis. In this thesis, we employed a Dynamic Photometric Analyzer (DPA) technique also known as the Rotating Analyzer Reflection Ellipsometer and the Static Photometric Ellipsometer techniques.

Ellipsometry is essentially a technique for determination of optical constants of a surface such as refractive index and thickness of thin films. Reflection ellipsometry enables to measure the refractive index and the thicknesses of thin films. The instrument relies on the fact that the reflection at the dielectric interface depends on the polarization of the light while the transmission of the light through the transparent layer changes the phase of the incoming wave depending on the refractive index of the material. The change of polarization in the state of polarization which is a characteristics of the reflecting surface is obtained by analyzing the reflected light. The ratio of the axes and the orientation of the reflected ellipse with respect to the plane parallel or perpendicular to the plane of incidence are determined [1]. An ellipsometer can be used to measure the layer thickness of the order of one nm to layers which are several micrometers. Applications include the accurate thickness measurement of thin films; the identification of materials and thin layer characteristics and extinction coefficients etc.

Chapter 1

ELECTROMAGNETIC WAVE EQUATION

The description of Ellipsometry as an optical technique would not be complete with out mentioning Maxwell's equations. Maxwell's theory predicts that light is an electromagnetic wave represented by two mutually perpendicular wave vectors, namely the electric field strength $\vec{E}$ and the magnetic field strength $\vec{B}$. Both are perpendicular to the direction of propagation. In the next section Maxwell's equations are explained in detail along with Fresnel's equations, Polarization of light, Stokes parameters and Jones vector calculus are also being reviewed.

1.1 Maxwell's Equations

The electromagnetic nature of wave propagating in a medium can be explained using Maxwell's equations. It shows that an electromagnetic field can propagate through a medium in the form of a wave. This also shows electromagnetic energy is conveyed by the electromagnetic wave. For simple consider a source free nonconducting medium characterized by ϵ, μ where ϵ, μ are permittivity and permeability of the medium respectively Maxwell's equations are given by

$$\nabla.\vec{D} = 0 \tag{1.1.1}$$

$$\nabla.\vec{B} = 0 \tag{1.1.2}$$

$$\nabla \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0 \tag{1.1.3}$$

$$\nabla \times \vec{H} - \frac{\partial \vec{D}}{\partial t} = 0. \tag{1.1.4}$$

The wave equations can be derived by taking the curl of Eqs.(1.1.3) and (1.1.4).and making appropriate substitutions i.e,

$$\nabla \times (\nabla \times \vec{E}) = -\frac{\partial}{\partial t}(\nabla \times \vec{B}) \tag{1.1.5}$$

$$\nabla(\nabla.\vec{E}) - \nabla^2\vec{E} = -\frac{\partial}{\partial t}(\mu(\nabla \times \vec{H})). \tag{1.1.6}$$

but

$$\nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} \tag{1.1.7}$$

Since $\nabla.\vec{E} = 0$

$$-\nabla^2\vec{E} = -\mu\frac{\partial^2}{\partial t^2}\vec{D} \tag{1.1.8}$$

again $\vec{D} = \epsilon\vec{E}$ we get

$$\nabla^2\vec{E} = \mu\epsilon\frac{\partial^2}{\partial t^2}\vec{E} \tag{1.1.9}$$

$$\nabla^2\vec{E} - \mu\epsilon\frac{\partial^2}{\partial t^2}\vec{E} = 0 \tag{1.1.10}$$

similarly using equation (1.1.4)we can obtain

$$\nabla^2\vec{B} - \mu\epsilon\frac{\partial^2}{\partial t^2}\vec{B} = 0 \tag{1.1.11}$$

equations (1.1.10) and (1.1.11) can be generalized as

$$\nabla^2\vec{U} - \mu\epsilon\frac{\partial^2}{\partial t^2}\vec{U} = 0 \tag{1.1.12}$$

where $\vec{U}$ represents $\vec{E}$ or $\vec{H}$. In general the solution of the above equation is

$$\vec{U} = U_0 exp(ik.z - i\omega t) \tag{1.1.13}$$

since

$$\frac{\partial}{\partial t} = -\imath\omega \tag{1.1.14}$$

and

$$\frac{\partial^2}{\partial t^2} = -\omega^2 \tag{1.1.15}$$

So Eq (1.1.12)can also be written as

$$\nabla^2\vec{U} + \frac{\omega^2}{v^2}\vec{U} = 0 \tag{1.1.16}$$

where $\mu\epsilon = \frac{1}{v^2}$ Eq(1.1.13)for the electromagnetic waves is expressed as

$$\vec{E} = \vec{E_0} exp(ik.z - i\omega t) \tag{1.1.17}$$

and

$$\vec{B} = \vec{B_0} exp(ik.z - i\omega t) \tag{1.1.18}$$

where E_0 and B_0 are constants in time and space. Each component must satisfy $k^2 n.n = \mu\epsilon\frac{\omega^2}{c^2}$. It can be shown that the $\vec{E}$ and $\vec{B}$ are both perpendicular to the direction of propagation or to the $\vec{k}$ from the dot product of $\vec{E}$ or $\vec{B}$ with the $\vec{k}$.

1.2 Reflection and Refraction at a Plane Boundary

Consider a plane harmonic wave which is incident on a plane boundary separating two different optical media as shown in figure 1.1. There will be reflected wave and transmitted wave. For a plane wave propagating in the z-direction and +x polarized the waves aside from constant amplitude factors is given by

$$\vec{E}(z,t) = \vec{E_0} exp(ik.z - i\omega t) \tag{1.2.1}$$

$$\vec{E'} = \vec{E'_0} exp(ik.z - i\omega t) \tag{1.2.2}$$

$$\vec{E"} = \vec{E"_0} exp(ik.z - i\omega t) \tag{1.2.3}$$

Where E,E' and $E"$ are the incident, reflected and transmitted electric waves. Similarly the incident, reflected and refracted magnetic waves are

$$\vec{B} = \vec{B_0} exp(ik.z - i\omega t) \tag{1.2.4}$$

$$\vec{B'} = \vec{B'_0} exp(ik.z - i\omega t) \tag{1.2.5}$$

$$\vec{B"} = \vec{B"_0} exp(ik.z - i\omega t) \tag{1.2.6}$$

We would like to compute the fraction of the light wave reflected and transmitted by a flat interface between two media with different refractive indices. Fresnel was the first to do this calculation. It proceeds by considering conditions at the interface for the electric and magnetic fields of the light wave. We will do for the perpendicular polarization first. The tangential component of $\vec{E}$ at the interface is continuous. Hence, for x-polarized light all $\vec{E}$ fields are in the z-direction which is in the plane of the interface(x,z),

$$\vec{E}(x, y = 0, z, t) + \vec{E'}(x, y = 0, z, t) = \vec{E"}(x, y = 0, z, t) \tag{1.2.7}$$

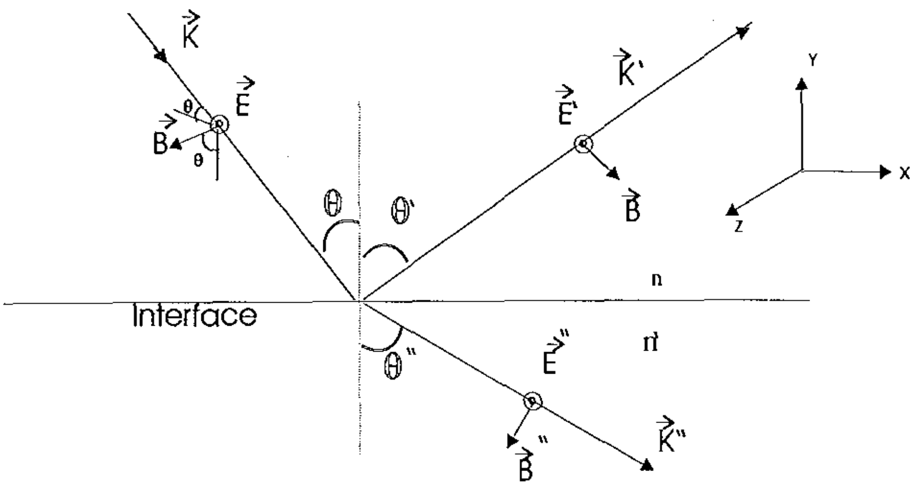

Figure 1.1: perpendicular polarization

Again the tangential component of the magnetic field is continuous, hence all $\vec{B}$ fields are in the xy plane. So we take the x-component

$$-\vec{B}(x, y=0, z, t)\cos\theta + \vec{B}'(x, y=0, z, t)\cos\theta' = -\vec{B}''(x, y=0, z, t)\cos\theta'' \quad (1.2.8)$$

At the boundary $z = 0$ Eq. (1.2.7) and Eq. (1.2.8) become

$$E_o + E_0' = E_0'' \quad (1.2.9)$$

$$-B_0\cos\theta + B_0'\cos\theta' = B_0''\cos\theta'' \quad (1.2.10)$$

But B=$\frac{NE}{c}$ and from laws of reflection

$$\theta = \theta' \quad (1.2.11)$$

$$N(E_0 - E_0')cos\theta = -N'E_0''cos\theta'' \quad (1.2.12)$$

From Eq1.2.9 and Eq. 1.2.10 we can get that

$$r_s = \frac{E_0'}{E_0} = \frac{N\cos\theta - N'\cos\theta''}{N\cos\theta + N'\cos\theta''} \quad (1.2.13)$$

Similarly

$$t_s = \frac{E_0^"}{E_0} = \frac{2N\cos\theta}{N\cos\theta + N'\cos\theta"} \tag{1.2.14}$$

In the second case for the parallel polarization the beam geometry for light with its electric field is parallel to the plane of incidence figure 1.2 below.

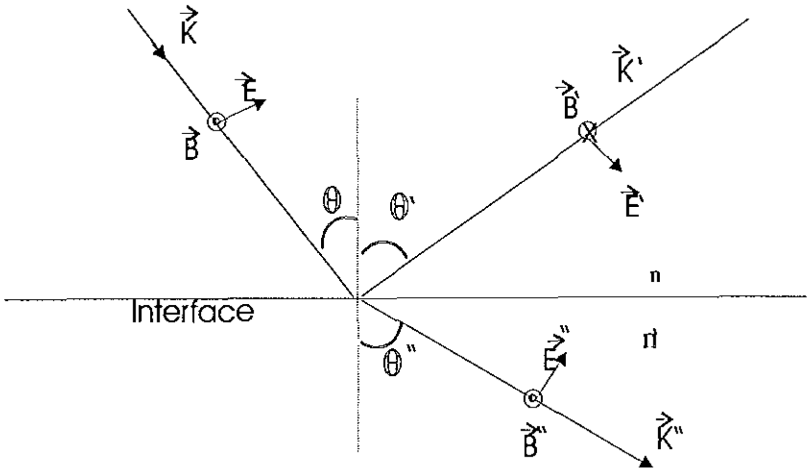

Figure 1.2: parallel polarization

Note that the reflected magnetic field must point in to the page to achieve $\vec{E} \times \vec{B}$ $\propto \vec{k}$

For parallel polarization still the tangential component of $\vec{B}$ and $\vec{E}$ are continuous.

$$B_o - B_0^{'} = B_0^{"} \tag{1.2.15}$$

and

$$E_0\cos\theta + E_0^{'}\cos\theta' = E_0^{"}\cos\theta" \tag{1.2.16}$$

solving for $\frac{E_0'}{E_0}$ yields

$$r_p = \frac{E_0^{'}}{E_0} = \frac{N\cos\theta" - N'\cos\theta}{N\cos\theta" + N'\cos\theta} \tag{1.2.17}$$

Similarly

$$t_p = \frac{E_0^"}{E_0} = \frac{2N\cos\theta}{N\cos\theta" + N'\cos\theta} \tag{1.2.18}$$

The Eqs 1.2.13, 1.2.14, 1.2.17 and 1.2, 18 are called Fresnel equations for perpendicular and parallel polarizations.

When a p-polarized wave is incident on the interface between two transparent media the reflected wave disappears at a particular angle of incidence called Brewster's angle θ_B, and the incident wave is totally refracted in to the second medium. So the refractive index can be related to the Brewster's angle as derived below.Equating $r_p = 0$ we get

$$N'\cos\theta = N\cos\theta" \tag{1.2.19}$$

from snell's law

$$N\sin\theta = N'\sin\theta" \tag{1.2.20}$$

and using the identity relation $\cos\theta" = \sqrt{1 - \frac{N^2}{N'^2}\sin^2\theta}$ we can obtain

$$\tan\theta_B = \frac{N'}{N} \tag{1.2.21}$$

Where the ratio $\frac{N'}{N}$ is real.

1.3 Reflection and Transmission by an Ambient-Film-Substrate System

The case of considerable importance in ellipsometry is that in which polarized light is reflected from, or transmitted by, a substrate covered by a single film as shown below.figure 1.3.

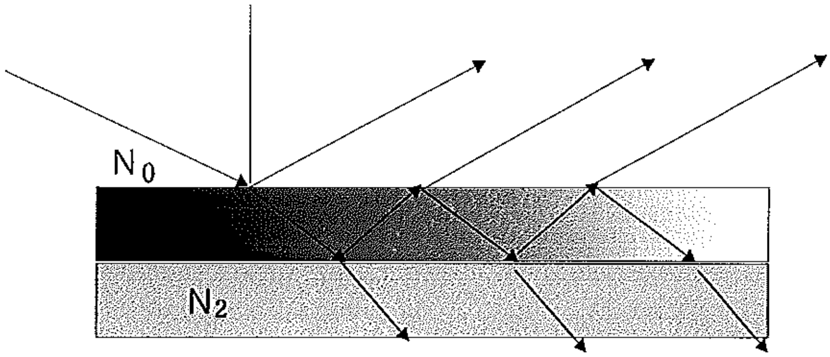

Figure 1.3: ambient-film-substrate fig

We assume that the film has parallel plane boundaries of separation (film thickness) d_1 and sandwiched between two semi-infinite ambient and substrate media. All the ambient-film and substrate are isotropic and homogenous with complex refractive indices of refraction N_0, N_1 and N_2 respectively. The medium 0 is transparent and N_0 is real.

A plane wave incident in medium 0 at an angle ϕ_0 will give rise to a resultant reflected wave in the same medium and resultant transmitted wave at ϕ_2 in medium 2 after suffering multiple internal reflections in the film. The Fresnel equations at the boundary $0-1, 1-0, 1-2$ are denoted by $r_{01}, t_{01} r_{10} t_{10}$ and $r_{12} t_{12}$ respectively.

The resultant reflected waves in medium 0 are given by [1, 10]

$$r_{o1}, t_{01}t_{10}r_{12}\exp -i2\beta, t_{01}t_{10}r_{10}r_{12}^2\exp -i4\beta, t_{01}t_{10}r_{10}^2 r_{12}^3\exp -i6\beta... \qquad (1.3.1)$$

while the transmitted waves in medium 2 are

$$t_{10}t_{12}\exp -i\beta, t_{10}t_{12}r_{10}r_{12}\exp -i3\beta, t_{10}t_{12}r_{10}^2 r_{12}^2\exp -i5\beta \qquad (1.3.2)$$

where

$$\beta = 2\pi(\frac{d_1}{\lambda})N_1\cos\phi_1 = 2\pi(\frac{d_1}{\lambda})(N_1^2 - N_0^2\sin^2\phi_0)^{\frac{1}{2}} \qquad (1.3.3)$$

so the total reflectance is

$$R = r_{01} + t_{01}t_{10}r_{12}\exp -i2\beta + t_{01}t_{10}r_{10}r_{12}^2\exp -i4\beta + ... \tag{1.3.4}$$

It is easy to show that Eq 1.3.4 can be written as

$$R = r_{01} + \frac{t_{01}t_{10}r_{12}\exp -i2\beta}{1 - r_{10}r_{12}\exp -i2\beta} \tag{1.3.5}$$

again using the relation $t_{01}t_{10}$=$1 - r_{01}^2$ and $r_{10} = -r_{01}$ Eq. 1.3.5 can be written in the form

$$R = \frac{r_{01} + r_{12}\exp -i2\beta}{1 + r_{01}r_{12}\exp -i2\beta} \tag{1.3.6}$$

similarly the transmittance T is

$$T = t_{01}t_{12}\exp -i\beta + t_{01}t_{12}r_{10}r_{12}\exp -i3\beta + ... \tag{1.3.7}$$

and this is the same as

$$T = \frac{t_{01}t_{12}\exp -i\beta}{1 + r_{01}r_{12}\exp -i3\beta} \tag{1.3.8}$$

Then the Fresnel coefficients for parallel and perpendicular polarizations are given by

$$R_P = \frac{r_{01p} + r_{12p}\exp -i2\beta}{1 + r_{01p}r_{12p}\exp -i2\beta} \tag{1.3.9}$$

$$R_s = \frac{r_{01s} + r_{12s}\exp -i2\beta}{1 + r_{01s}r_{12s}\exp -i2\beta} \tag{1.3.10}$$

$$T_P = \frac{t_{01p}t_{12p}\exp -i\beta}{1 + r_{01p}r_{12p}\exp -i3\beta} \tag{1.3.11}$$

$$T_s = \frac{t_{01s}t_{12s}\exp -i\beta}{1 + r_{01s}r_{12s}\exp -i3\beta} \tag{1.3.12}$$

1.4 The Concept Of Polarization

Polarization is a property that is common to all types of vector waves. Electromagnetic waves also possess this property. For all types of vector waves polarization refers to the behavior with time of one of the field vectors appropriate to the wave observed at a fixed point in space.

Light waves are electromagnetic in nature and require four basic field vectors for their complete description. These are the electric field strength $\vec{E}$, the magnetic field strength $\vec{H}$, the electric displacement density $\vec{D}$ and the magnetic flux density $\vec{B}$. Out of these four vectors, the electric field strength $\vec{E}$ is chosen to define the state of polarization of light waves. This choice is based on the fact that when light interacts with matter, the force exerted on the electrons by the electric field of the wave is much greater than the force exerted on the electrons by the magnetic field of the wave. In general once the polarization of $\vec{E}$ has been determined the polarization of $\vec{B}$, $\vec{H}$ and $\vec{D}$ can be found. This is because $\vec{E}$, $\vec{B}$, $\vec{H}$ and $\vec{D}$ are interrelated by Maxwell's equations. So we can define polarization of light as the behavior of electric vector $\vec{E}(r,t)$ observed at a fixed point in space $\vec{r}$, and time, t.

1.4.1 Linear Polarization

Consider two orthogonal optical disturbances these are

$$E_x(z,t) = \mathrm{i}E_{ox}\cos(kz - \omega t) \tag{1.4.1}$$

$$E_y(z,t) = \mathrm{j}E_{oy}\cos(kz - \omega t + \varepsilon) \tag{1.4.2}$$

where ε is the relative phase difference between the wave both are travelling in the z-direction. Since the phase is in the form of $(kz - \omega t)$, the addition of positive ε

means that the cosine function in Eq. (1.4.2) will not attain the same value as the cosine function in Eq. (1.4.1) until the later time $(\frac{\varepsilon}{\omega})$. Accordingly E_y lags E_x by $\varepsilon > 0$. Of course, if ε is negative quantity, E_y leads E_x by $\varepsilon < 0$. The resultant optical disturbance is the the vector some of these two perpendicular waves.

$$\vec{E}(z,t) = E_x(z,t) + E_y(z,t) \tag{1.4.3}$$

If ε is zero or an integer multiple of $\pm 2\pi$,the waves are said to be in phase. In this case Eq. (1.3.3) becomes

$$\vec{E}(z,t) = (\mathbf{i}E_{ox} + \mathbf{j}E_{oy})\cos(kz - \omega t) \tag{1.4.4}$$

The resultant wave has a fixed amplitude equal to $\sqrt{E_{ox}^2 + E_{oy}^2}$. i.e the wave is linearly polarized. Suppose that ε is an odd integer multiple of $\pm\pi$, the two waves are out of phase by 180^0. And the wave is

$$\vec{E}(z,t) = (\mathbf{i}E_{ox} - \mathbf{j}E_{oy})\cos(kz - \omega t) \tag{1.4.5}$$

This wave is again linearly polarized but plane of polarization has been rotated from that of the previous condition.

1.4.2 Circular Polarization

Another case of particular interest arises when both constituent waves have equal amplitude, i.e, E_{0x}=E_{0y}=E_0 and in addition, their relative phase difference is $\varepsilon = -\frac{\pi}{2}+2m\pi$ where,$m = 0, \pm 1 \pm 2 \pm 3...$ Now Eqs. (1.3.1) and(1.3.2) become

$$E_x(z,t) = \mathbf{i}E_0\cos(kz - \omega t) \tag{1.4.6}$$

$$E_y(z,t) = \mathbf{j}E_o\cos(kz - \omega t + \varepsilon) \tag{1.4.7}$$

So the resultant wave is

$$\vec{E}(z,t) = E_0[\mathbf{i}\cos(kz - \omega t) + \mathbf{j}\sin(kz - \omega t)] \tag{1.4.8}$$

Now the scalar amplitude E_0 is constant and the direction of $\vec{E}$ is time varying and not restricted as before on a single plane, for example at $t = 0$

$$E_x = \mathrm{i}E_o\cos(kz_o) \ and \ E_y = \mathrm{j}E_o\sin(kz_o) \tag{1.4.9}$$

At later time $t = \frac{kz_0}{\omega}$,

$$E_x = \mathbf{i}E_0, \ E_y = 0 \tag{1.4.10}$$

. i.e, $\vec{E}$ is along the x-axis. The resultant electric field vector $\vec{E}$ is rotating clockwise at an angular frequency of ω, as seen by an observer against the wave propagation direction (i.e, looking back at the source). Such a wave is called right circular polarization.

The $\vec{E}$ makes one complete rotation as the wave advances through one wavelength. In comparison if $\varepsilon = \frac{\pi}{2} + 2m\pi$ where $m = 0, \pm 1, \pm 2, ...$ Then

$$\vec{E} = E_0[\mathrm{i}\cos(kz - \omega t) - \mathrm{j}\sin(kz - \omega t)] \tag{1.4.11}$$

The amplitude is constant, but $\vec{E}$ now rotates counterclockwise and the wave is left circular polarization. A linearly polarized wave can be synthesized from two oppositely polarized circular waves of equal amplitude. In particular, if we add the right circular wave to the left circular wave of equal amplitude we get

$$\vec{E} = \mathrm{i}2E_0\cos(kz - \omega t) \tag{1.4.12}$$

This shows a linearly polarized wave of amplitude $2E_0$ in the direction of i

1.4.3 Elliptical Polarization

A light wave whose electric vector at a fixed point in space traces the same ellipse in a regular repetitive fashion is described as elliptical polarization at that point. To understand elliptical polarization we can see this better by actually writing an expression for the curve traversed by the tip of $\vec{E}$. To that end; recall that

$$E_x = E_{0x}\cos(kz - \omega t) \tag{1.4.13}$$

$$E_y = E_{0y}\cos(kz - \omega t + \varepsilon) \tag{1.4.14}$$

The equation we are looking for should not be a function of either position or time. In other words we should be able to get rid of $(kz - \omega t)$ dependance. So expanding for E_y into

$$\frac{E_y}{E_{0y}} = \cos(kz - \omega t + \varepsilon) = \cos(kz - \omega t)\cos(\varepsilon) - \sin(kz - \omega t)\sin(\varepsilon) \tag{1.4.15}$$

From Eq. 1.4.13 we have $\cos(kz - \omega t) = \frac{E_x}{E_{ox}}$. So

$$\frac{E_y}{E_{0y}} = \frac{E_x}{E_{0x}}\cos(\varepsilon) - \sin(kz - \omega t)\sin(\varepsilon) \tag{1.4.16}$$

$$\frac{E_y}{E_{0y}} - \frac{E_x}{E_{0x}}\cos(\varepsilon) = -\sin(kz - \omega t)\sin(\varepsilon) \tag{1.4.17}$$

But using Eq. (1.4.13) and the trigonometric identity $\cos^2(kz-\omega t)+\sin^2(kz-\omega t) = 1$, Eq. (1.4.17) becomes

$$\frac{E_y^2}{E_{0y}^2} + \frac{E_x^2}{E_{0x}^2}\cos^2(\varepsilon) - \frac{2E_yE_x\cos(\varepsilon)}{E_{0x}E_{0y}} + (\frac{E_x}{E_{0x}})^2\sin^2(\varepsilon) = \sin^2(\varepsilon) \tag{1.4.18}$$

$$\frac{E_y^2}{E_{0y}^2} + \frac{E_x^2}{E_{0x}^2} - \frac{2E_yE_x\cos(\varepsilon)}{E_{0y}E_{0x}} = \sin^2(\varepsilon) \tag{1.4.19}$$

Eq.(1.4.19) shows equation of ellipse making an angle α with the (E_x, E_y) coordinate system such that

$$\tan(2\alpha) = \frac{2E_{0x}E_{0y}\cos(\varepsilon)}{E_{0x}^2 - E_{0y}^2} \tag{1.4.20}$$

If $\varepsilon = \frac{\pi}{2}$ and $E_{0x} = E_{0y} = E_0$, then Eq. (1.4.19) becomes

$$E_y^2 + E_x^2 = E_0^2 \tag{1.4.21}$$

1.5 Stokes Parameters

The modern representation of polarized light actually had its origin, in 1852, the work reported by G.G. Stokes. He introduced four observable quantities of the electromagnetic waves and are known as Stokes parameters. So the polarization state of light can be described by these quantities. The operational definition of Stokes parameters is then given by the relations

$$S_0 = 2I_0 \tag{1.5.1}$$

$$S_1 = 2I_1 - 2I_0 \tag{1.5.2}$$

$$S_2 = 2I_2 - 2I_0 \tag{1.5.3}$$

$$S_3 = 2I_3 - 2I_0 \tag{1.5.4}$$

Notice that S_0 is the incident irradiance and S_1, S_2, S_3 are the state of polarizations. Thus S_1 refers a tendency for the polarization to resemble either a horizontal P-state (where upon $S_1 > 0$) or vertical one in which case $S_1 < 0$. When the beam reflects no preferential orientation with respect to these axes $S_1 = 0$, it may be elliptical at $\frac{\pi}{4}$ when $S_2 > 0$, or in the direction of $-\frac{\pi}{4}$ when $S_2 < 0$ or neither if $S_2 = 0$. In the same way S_3 resembles a tendency of the beam towards right handedness if $S_3 > 0$ and left handedness if $S_3 < 0$, and neither if $S_3 = 0$. Given

$$\vec{E_x}(t) = \mathbf{i}E_{ox}(t)\cos[(kz - \omega t) + \varepsilon_x(t)] \tag{1.5.5}$$

$$\vec{E_y}(t) = \mathbf{j}E_{oy}(t)\cos[(kz - \omega t) + \varepsilon_y(t)] \tag{1.5.6}$$

with $\vec{E}(t) = \vec{E_{x(t)}} + \vec{E_{y(t)}}$. Then the Stokes parameters are

$$S_0 = \langle E_{0x}^2 \rangle_T + \langle E_{0y}^2 \rangle_T \tag{1.5.7}$$

$$S_1 = \langle E_{ox}^2 \rangle_T - \langle E_{oy}^2 \rangle_T \tag{1.5.8}$$

$$S_2 = \langle 2E_{ox}E_{oy}\cos(\varepsilon) \rangle_T \tag{1.5.9}$$

$$S_3 = \langle 2E_{ox}E_{oy}\sin(\varepsilon) \rangle_T \tag{1.5.10}$$

where $\varepsilon = \varepsilon_y - \varepsilon_x$. Therefore the parameters are proportional to the irradiance. For perfectly monochromatic light $E_{0x}(t), E_{0y}(t)$, and $\varepsilon(t)$ are time independent. The same result can be obtained by time averaging which is the general equation for elliptical light. If the beam is unpolarized,

$$\langle E_{ox}^2 \rangle_T = \langle E_{oy}^2 \rangle_T \tag{1.5.11}$$

In this case

$$S_o = \langle E_{ox}^2 \rangle_T + \langle E_{oy}^2 \rangle_T \tag{1.5.12}$$

but $S_1 = S_2 = S_3 = 0$ since the average of $\cos(\varepsilon)$ and $\sin(\varepsilon) = 0$. To normalize the Stokes parameters divide by S_0. So, for the unpolarized light the state of Stokes parameters (S_0, S_1, S_2, S_3) are

$$(1, 0, 0, 0). \tag{1.5.13}$$

If the light is horizontally polarized, it has no vertical component of E; i.e, $E_{0y} = 0$. Thus for the parameters $S_0 = \langle E_{ox}^2 \rangle_T, S_1 = \langle E_{ox}^2 \rangle_T, S_2 = 0, S_3 = 0$ the state becomes

$$(1, 1, 0, 0) \tag{1.5.14}$$

For the vertical polarization, $S_0 = \langle E_{oy}^2 \rangle_T, S_1 = -\langle E_{oy}^2 \rangle_T, S_2 = 0, S_3 = 0$ thus

$$(1, -1, 0, 0) \tag{1.5.15}$$

For completely polarized light $S_0^2 = S_1^2 + S_2^2 + S_3^2$. For partially polarized light it can be shown that the degree of polarization is given by $v = \frac{\sqrt{S_1^2+S_2^2+S_3^2}}{S_0}$. Consider non chromatic waves described by (S_0, S_1, S_2, S_3) and $(S_0^{'}, S_1^{'}, S_2^{'}, S_3^{'})$ which are superimposed in some region of space, as long as the wave is incoherent, any one of the Stokes parameters of the resultant will be the sum of the corresponding parameters of the constituent (all of which are proportional to the irradiance).

The set of Stokes parameters for a given wave can be rewritten as a vector. Its representation is more specifically the parameters (S_0, S_1, S_2, S_3) are arranged in the form of column vector which is called Stokes vector [10]. I.e,

$$S = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix}$$

Some examples of Stokes vector are

Unpolarized light $S = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$

$$\text{Horizontal P-state } S = \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix}$$

$$\text{Vertical P-state } S = \begin{pmatrix} 1 \\ -1 \\ 0 \\ 0 \end{pmatrix}$$

$$\text{P-state at } \tfrac{+\pi}{4} \; S = \begin{pmatrix} 1 \\ 0 \\ 1 \\ 0 \end{pmatrix}$$

$$\text{P-state at } \tfrac{-\pi}{4} \; S = \begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix}$$

$$\text{R-state } S = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\text{L-state } S = \begin{pmatrix} 1 \\ 0 \\ 0 \\ -1 \end{pmatrix}$$

1.6 THE Jones Vectors

Another representation of polarized light is invented by the American Physicist R. Clark Jones. First let us represent the beam in terms the electric vector itself written in column vector. That is the Jones vector is [4, 10]

$$\vec{E} = \begin{pmatrix} E_{ox}\exp(i\varphi_x) \\ E_{oy}\exp(i\varphi_y) \end{pmatrix} \tag{1.6.1}$$

Where φ_x and φ_y are appropriate phases. The horizontal and vertical P-states are given by

$$\tilde{E} = \begin{pmatrix} E_{ox}\exp(i\varphi_x) \\ 0 \end{pmatrix} \tag{1.6.2}$$

$$\vec{E} = \begin{pmatrix} 0 \\ E_{oy}\exp(i\varphi_y) \end{pmatrix} \tag{1.6.3}$$

respectively. Then any vector $\vec{E}$ can be equivalently written in the two forms as

$$\vec{E} = \mathbf{i}E_{ox}\exp(i\varphi_x) + \mathbf{j}E_{oy}\exp(i\varphi_x) \Leftrightarrow \vec{E} = \begin{pmatrix} E_{ox}\exp(i\varphi_x) \\ E_{oy}\exp(i\varphi_y) \end{pmatrix} \tag{1.6.4}$$

For $E_{ox} = E_{oy}$ and $\varphi_x = \varphi_y = \varphi$, Eq. (1.6.4) can be written as

$$\vec{E} = E_{ox}\exp(i\varphi)\begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{1.6.5}$$

which is a P-state at $+\frac{\pi}{4}$ i.e, the amplitudes are equal and phase difference is 0.

If $E_{ox} \neq E_{oy}$, it is possible to normalize and this is done by dividing both elements in the vector by the same scalar; i.e, the some of components is unity. Or

$$E_{ox}^2 + E_{oy}^2 = 1 \tag{1.6.6}$$

For example; if

$$\vec{E} = \mathbf{i}E_{ox}\exp(i\varphi_x) + \mathbf{j}E_{ox}\exp(i\varphi_x) \tag{1.6.7}$$

Dividing Eq.(1.5.7) by $\sqrt{2}E_{ox}\exp(i\varphi_x)$, we get

$$\vec{E}_{\frac{\pi}{4}} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} \Rightarrow \vec{E}_h = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} and \vec{E}_v = \frac{1}{\sqrt{2}}\begin{pmatrix} 0 \\ 1 \end{pmatrix} \tag{1.6.8}$$

For right circular polarization $E_{ox} = E_{oy}$ and the y-component leads the x-component by $\frac{\pi}{2}$. I.e,

$$\hat{E} = \begin{pmatrix} E_{0x}\exp(i\varphi_x) \\ E_{0x}\exp(i\varphi_x - \frac{\pi}{2}) \end{pmatrix} = E_{0x}\exp(i\varphi)\begin{pmatrix} 1 \\ \exp(i\frac{-\pi}{2}) \end{pmatrix} \tag{1.6.9}$$

Dividing Eq. (1.5.9) by $E_{ox}\exp(i\varphi)$, we get

$$\begin{pmatrix} 1 \\ \exp(i\frac{-\pi}{2}) \end{pmatrix} = \begin{pmatrix} 1 \\ -i \end{pmatrix} \tag{1.6.10}$$

Hence the normalized complex Jones vector is

$$\tilde{E_R} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \end{pmatrix} and \tilde{E_L} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \end{pmatrix} \tag{1.6.11}$$

The sum of right circular and left circular polarization is

$$\tilde{E_R} + \tilde{E_L} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1+1 \\ -i+i \end{pmatrix} = \frac{2}{\sqrt{2}}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{1.6.12}$$

Which shows horizontal P-state having an amplitude $2E_{ox}$. The same procedure is done for elliptical polarization. In this case $E_{ox} \neq E_{oy}$ and phase difference need not be $\frac{\pi}{2}$.

Chapter 2

THEORY OF ELLIPSOMETRY AT A PLANE BOUNDARY

In this chapter we will discuss the methods employed for the determination of optical constants of the conducting polymer using ellipsometric techniques called the Dynamic Photometric ellipsometer particularly the Rotating analyzer and the static photometric ellipsometry technique. The method we use are explained in detail below.

2.1 Introduction

In this topic we will see the relationship between the ellipsometric parameters ψ , Δ and Fresnel equations enable us to build an equation which helps us to calculate the refractive index of the polymer sample.

An ellipsometric measurement allows one to quantify the phase difference between E_P and E_S, Δ, and the change in the ratio of there amplitudes given by $\tan\psi$.
I.e., $\Delta = \delta_{rp} - \delta_{rs}$ and $\tan\psi = \frac{|r_p|}{|r_s|}$ where r_p and r_s are Fresnel coefficients for P and S components of the light.

Now, conventional reflection ellipsometry measures the change of state of polarization of light as it is reflected from a surface. The change in state of polarization which is a characteristic of the reflecting surface, is obtained by analyzing the reflected light, the ratio of the axes and the orientation of the reflected ellipse with respect to the plane parallel or perpendicular to the plane of incidence are determined [1, 2, 3].

The r_p and r_s polarizations can be related to the ellipsometric angles ψ and Δ, such that at a plane boundary

$$\rho = \tan\psi \exp i\Delta \tag{2.1.1}$$

where ρ is the ratio r_p to r_s, i.e.,

$$\rho = \frac{|r_p|}{|r_s|} \tag{2.1.2}$$

where

$$r_p = \frac{N_1\cos\theta_0 - N_0\cos\theta_1}{N_1\cos\theta_0 + N_0\cos\theta_1}$$

and

$$r_s = \frac{N_0\cos\theta_0 - N_1\cos\theta_1}{N_0\cos\theta_0 + N_1\cos\theta_1}$$

So Eq. 2.1.2 can be written as

$$\rho = \frac{\left(\frac{N_1\cos\theta_0 - N_0\cos\theta_1}{N_1\cos\theta_0 + N_0\cos\theta_1}\right)}{\left(\frac{N_0\cos\theta_0 - N_1\cos\theta_1}{N_0\cos\theta_0 + N_1\cos\theta_1}\right)} \tag{2.1.3}$$

From Snell's law

$$N_1\sin\theta_1 = N_0\sin\theta_0$$

So solving for $\sin\theta_1$

$$\sin\theta_1 = \frac{N_0\sin\theta_0}{N_1} \tag{2.1.4}$$

Now using snell's law and trigonometric identity we can get

$$\cos\theta_1 = \frac{\sqrt{N_1^2 - \sin^2\theta_0}}{N_1} \tag{2.1.5}$$

Inserting Eq. 2.1.5 in to Eq. 2.1.3 and solving for $N = \frac{N_1}{N_0}$ we get

$$N = \sin\theta_0[1 + (\frac{1-\rho}{1+\rho})^2 \tan^2\theta_0]^{\frac{1}{2}} \tag{2.1.6}$$

Since $N_0 = 1$ which is the refractive index of air then $N = N_1$ where $N = n - ik$ which is complex refractive index of the polymer sample. For a material whose refractive index is real, then the complex refractive index can be expressed using its real part $Re\{N\} = n$ and

$$\rho = \tan\psi\cos\Delta \tag{2.1.7}$$

while for a material where $N = n - ik$, $\rho = \tan\psi \exp i\Delta$. Substituting the expressions of N and ρ into equation (2.1.6), and squaring both sides and separating real and imaginary parts [8]

$$n^2 - k^2 = \sin^2\theta_0\{1 + \frac{\tan^2\theta_0(\cos^2 2\psi - \sin^2 2\psi\sin^2\Delta)}{(1+\sin 2\psi\cos\Delta)^2}\} \tag{2.1.8}$$

and

$$2nk = \frac{\sin^2\theta_0\tan^2\theta_0\sin 2\psi\sin\Delta}{(1+\sin 2\psi\cos\Delta)^2} \tag{2.1.9}$$

2.2 Ellipsometry and Polarized Light

A light from the source falls on the polarizer which is set at the azimuth angle P with respect to the x-axis. This means that the transmission angle of the polarizer makes an angle P from the x-axis of the x-y coordinate of the light. The light incident on the x-y coordinate plane is

$$E_{p_i}^{xy} = \begin{pmatrix} \cos(P) & \sin(P) \\ -\sin(P) & \cos(P) \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} \tag{2.2.1}$$

this implies

$$E_{p_i}^{xy} = \begin{pmatrix} E_x \cos(P) + E_y \sin(P) \\ -E_x \sin(P) + E_y \cos(P) \end{pmatrix} \tag{2.2.2}$$

Only light having polarization parallel to the transmission axis of the polarizer will comes out. In the transmission extinction axis, the electric field which comes out from the polarizer is

$$E_{P_o}^{te} = T_P^{te} E_{P_i}^{xy} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} E_x \cos(P) + E_y \sin(P) \\ -E_x \sin(P) + E_y \cos(P) \end{pmatrix} \tag{2.2.3}$$

$$E_{P_o}^{te} = \begin{pmatrix} E_{P_o}^{t} \\ E_{P_o}^{e} \end{pmatrix} = \begin{pmatrix} E_x \cos(P) + E_y \sin(P) \\ 0 \end{pmatrix} = A_P \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.2.4}$$

where $E_{po}^{te} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ is the Jones matrix of polarizer and A_P is the amplitude of transmitted light wave.

$$A_P = E_x \cos(P) + E_y \sin(P) \tag{2.2.5}$$

This transmitted wave from the polarizer can be transmitted into xy -coordinate axes so that light incident on the optical system (sample) can be treated in the x-y coordinate axes. This can be done by counter rotation of the polarized light wave in Eq. (2.2.4) for angle P. The light wave incident on the sample is then

$$E_{si}^{xy} = R(-P) E_{P_o}^{te} = A_P \begin{pmatrix} \cos(P) & -\sin(P) \\ \sin(P) & \cos(P) \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{2.2.6}$$

$$E_{si}^{xy} = A_P \begin{pmatrix} \cos(P) \\ \sin(P) \end{pmatrix} \tag{2.2.7}$$

The light expressed by Eq. (2.2.7) is now incident on the sample. The Jones vector of the light wave at the out put of the optical system is related to that of the input by

$$E_{so}^{xy} = T_s^{xy} E_{si}^{xy} \tag{2.2.8}$$

The optical system is assumed to have orthogonal eigen polarization parallel to the x and y coordinates axes so that the Jones matrix has diagonal value T_s^{xy} [1].

$$T_s^{xy} = \begin{pmatrix} V_{ex} & 0 \\ 0 & V_{ey} \end{pmatrix} = |V_{ey}| \begin{pmatrix} \rho & 0 \\ 0 & 1 \end{pmatrix} \tag{2.2.9}$$

where

$$\rho = \frac{V_{ex}}{V_{ey}} = \tan\psi \exp(i\Delta) \tag{2.2.10}$$

is the complex polarization variable, which is the ratio of the eigen values of the reflected light along the x-direction to the y-direction. Using Eqs. (2.2.7) and (2.2.9), Eq. (2.2.8) can be written as

$$E_{so}^{xy} = A_P |(V_{ey})| \begin{pmatrix} \rho & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \cos(P) \\ \sin(P) \end{pmatrix} \tag{2.2.11}$$

The complex polarization variable, χ_{so}^{xy}, of the light wave reflected from the sample is

$$\chi_{so}^{xy} = \frac{E_{so}^y}{E_{so}^x} = \frac{\sin(P)}{\rho\cos(P)} = \frac{1}{\rho}\tan(P) \tag{2.2.12}$$

The light reflected from the sample, Eq.(2.2.11), will then be analyzed by the analyzer that is at the azimuth angle A, from the axis, then the light incident on the analyzer in its transmission extinction (t_e) axis is:

$$E_{AI}^{t_e} = R(A) E_{AI}^{xy} \tag{2.2.13}$$

but $E^{xy}_{AI} = E^{xy}_{so}$, then

$$E^{t_e}_{AI} = A_P|V_{ey}|\begin{pmatrix} \cos(A) & \sin(A) \\ \sin(A) & \cos(A) \end{pmatrix}\begin{pmatrix} \rho\cos(P) \\ sin(P) \end{pmatrix} \quad (2.2.14)$$

$$E^{t_e}_{AI} = A_P|V_{ey}|\begin{pmatrix} \rho\cos(P)\cos(A) + \sin(P)\sin(A) \\ \rho\cos(P)\sin(A) + \sin(P)\cos(A) \end{pmatrix} \quad (2.2.15)$$

Then the light wave emergent from the analyzer is related to its input by

$$E^{t_e}_{Ao} = T^{t_e}_{A} E^{t_e}{}_{AI} \quad (2.2.16)$$

Since only light wave parallel to the trausmission axis of the analyzer is allowed to pass through, the Jones matrix of the analyzer is diagonal; i.e $T^{t_e}_{A}=\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ then Eq. (2.2.16) will take the form

$$E^{t_e}_{Ao} = A_P|V_{ey}|\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}\begin{pmatrix} \rho\cos(P)\cos(A) + \sin(P)\sin(A) \\ \rho\cos(P)\sin(A) + \sin(P)\cos(A) \end{pmatrix} \quad (2.2.17)$$

$$E^{t_e}_{Ao} = A_P|V_{ey}|\begin{pmatrix} \rho\cos(P)\cos(A) + \sin(P)\sin(A) \\ 0 \end{pmatrix} \quad (2.2.18)$$

Then the electric field at the detector or Lock-In amplifier is similar to the field emergent from the analyzer. But for mathematical convenience we can write this field in x-y coordinate for the counter rotation from the x-axis as [1]

$$E^{xy}_{d} = R(-A)E^{t_e}_{Ao} \quad (2.2.19)$$

$$E^{xy}_{d} = A_P|(V_{ey})|\begin{pmatrix} \cos(A) & -\sin(A) \\ \sin(A) & \cos(A) \end{pmatrix}\begin{pmatrix} \rho\cos(P)\cos(A) + \sin(P)\sin(A) \\ 0 \end{pmatrix} \quad (2.2.20)$$

$$E^{xy}_{d} = A_P|(V_{ey})|\begin{pmatrix} \rho\cos(P)\cos^2(A) + \sin(P)\sin(A)\cos(A) \\ \cos(P)\cos(A)\sin(A) + \sin(P)\sin^2(A) \end{pmatrix} \quad (2.2.21)$$

The intensity of the detected signal I_d at the detector is related to the field at its position by; $I_d \ \alpha \ E^{+}_{Ao_t} E_{o_t}$ since $E^{+}_{Ao} = E_{Ao_t}$ then

$$I_d = K_d|E^{+}_{Ao}|^2 = K_o|A_P|^2|V_{ey}|^2|\rho \cos(P)\cos(A) + \sin(P)\sin(A)|^2 \tag{2.2.22}$$

But ρ is a complex polarization variable given by eq. (2.2.10) then

$$I_d = G|\tan\psi \exp(i\Delta)\cos(p)\cos(A) + \sin(P)\sin(A)|^2 \tag{2.2.23}$$

where $G = |A_P|^2 K_d |V_{ey}|^2 = constant$ then Eq. (2.2.23) becomes

$$I_d = G[\sin^2(P)\sin^2(A) + \cos^2(P)\cos^2(A)\tan^2(\psi) + 2\cos(P)\cos(A)\sin(P)\sin(A)\tan(\psi)\cos(\Delta)] \tag{2.2.24}$$

But $\sin^2(A) = \frac{1-\cos(2A)}{2}$, $\cos^2(A) = \frac{1+\cos(2A)}{2}$ and $\cos(2A) = 2\cos(A)\sin(A)$ then using the above identity Eq. (2.2.24) can be written as

$$I_d = G[C + \alpha' \cos(2A) + \beta' \sin(2A)] \tag{2.2.25}$$

or this can also be written as

$$I_d = \bar{I}_d[1 + \alpha\cos(2A) + \beta\sin(2A)] \tag{2.2.26}$$

where

$$C = \frac{\sin^2(P)}{2} + \frac{\cos^2(P)}{2}\tan^2(\psi) \tag{2.2.27}$$

$$\alpha = \frac{\cos^2(P)\tan^2(\psi) - \sin^2(p)}{2C} \tag{2.2.28}$$

$$\beta = \frac{\cos(P)\sin(P)\tan(\psi)\cos(\Delta)}{C} \tag{2.2.29}$$

The relation between α and β with the ellipsometric parameters ψ and Δ is given below. Now α and β are constants to be determined from curve fitting of Eq. (2.2.25), i.e, using Eqs. $(2.2.26), (2.2.27), and (2.2.28)$ we can get the following relations

$$\tan\psi = \sqrt{\frac{1+\alpha}{1-\alpha}}\tan(P) \tag{2.2.30}$$

$$\cos\Delta = \frac{\beta}{\sqrt{1-\alpha^2}} \tag{2.2.31}$$

2.3 Static Photometric Ellipsometry

In principle, no compensator is required for the determination of the ellipsometric parameters ψ and Δ by photometric methods [1]. It is, there fore, reasonably good to consider the Polarizer-System-Analyzer (PSA) Ellipsometer arrangement. The detected signal I_d is a function of angle P of the polarizer and A of the angle of the analyzer that can be readily obtained by setting $C = 0$ and $T_c \exp(i\delta_c) = 1$ in the equation expressed bellow [1].

$$\begin{aligned} I_d &= G|V_{ey}|^2|\tan\psi \exp i\Delta \cos A[\cos C\cos(P-C) - T_c\exp(i\delta_c)\sin c \sin(P-C)] + \\ &\quad \sin A[\sin C\cos(P-C) + T_c\exp(i\delta_c)\cos C\sin(P-C)]|^2 \end{aligned} \tag{2.3.2}$$

this can be written as

$$G|V_{ey}|^2[(\tan\psi\exp i\Delta\cos A\cos P + \sin A\sin P)(\tan\psi\exp -i\Delta\cos A\cos P + \sin A\sin P)] \tag{2.3.3}$$

Expanding Eq. 2.3.2 and using the trigonometric identities $\cos^2 A = \frac{1+\cos 2A}{2}$ and $\sin^2 A = \frac{1-\cos 2A}{2}$ and so on we get

$$I_d = F'[1 - \cos 2\psi(\cos 2A + \cos 2P) + \cos 2A\cos 2P + \sin 2\psi\sin 2A\sin^2 P\cos\Delta] \tag{2.3.4}$$

Let I_{d1},I_{d2}, I_{d3} are the detected signals at three different sets (P_1, A_1), (P_2, A_2) and (P_3, A_3) of polarizer analyzer azimuth angles, substitution of the data in to Eq. 2.3.3 produces three equations in $F^{'}$, ψ and Δ. Dividing the first and second equations by the third eliminates $F^{'}$, and gives two equations that can be solved for the two ellipsometric parameters ψ and Δ. Measurement of ψ and Δ from photometric data using a PSA ellipsometer can be done by setting (P,A) for the polarizer and analyzer azimuth angles left arbitrary. One choice that simplifies data reduction is to set the polarizer at a fixed azimuth of $\frac{\pi}{4}$ and recorded the signals I_d at the three analyzer settings,$\frac{-\pi}{4}$, 0 and $\frac{\pi}{4}$ and inserting on Eq. 2.3.3 we get the following Eqs. [1]

$$I_{d1} = I_d(\frac{\pi}{4}, \frac{-\pi}{4}) = F^{'}(1 - \sin 2\psi \cos \Delta) \tag{2.3.5}$$

$$I_{d2} = I_d(\frac{\pi}{4}, 0) = F^{'}(1 - cos2\psi) \tag{2.3.6}$$

$$I_{d3} = I_d(\frac{\pi}{4}, \frac{\pi}{4}) = F^{'}(1 + \sin 2\psi \cos \Delta) \tag{2.3.7}$$

So using Eqs. 2.3.5, 2.3.6 and 2.3.7 the values of ψ and Δ are:

$$\psi = \frac{1}{2} \arccos [\frac{I_{d1} + I_{d3} - 2I_{d2}}{I_{d1} + I_3}] \tag{2.3.8}$$

$$\Delta = \arccos [\csc 2\psi (\frac{I_{d3} - I_{d1})}{I_{d3} + I_{d1}}] \tag{2.3.9}$$

Chapter 3

EXPERIMENTAL RESULT AND DISCUSSION

3.1 Sample preparation and its nature

The polymer thin film under study was prepared from a chloroform solution of $poly[3-(4-octylphenyl)-2,2'-bithiophene]$ (PTOPT) by spin coating on a glass substrate. The spin coating was done using a photo resist spinner model 4000 at a rate of 1000 rpm. The film thickness is measured using a talystep. From the way how the sample was prepared, we expect that the film is homogeneous and isotropic medium.

Our sample is ambient-film -substrate system, so we expect reflection from the back surface. But, as measurement of transmission shows, for all wavelengths greater than 600 nm the sample is highly transparent and having transmission around .98 (see figure 3.1). So, the problem can be treated as a one boundary problem, i.e, the relation used for one boundary problem can be applied for our sample to calculate the refractive index [3].

The graph in Figure 3.1 below shows wavelength in nm versus transmittance.

The sample was clear and optically transparent and homogeneous. This shows

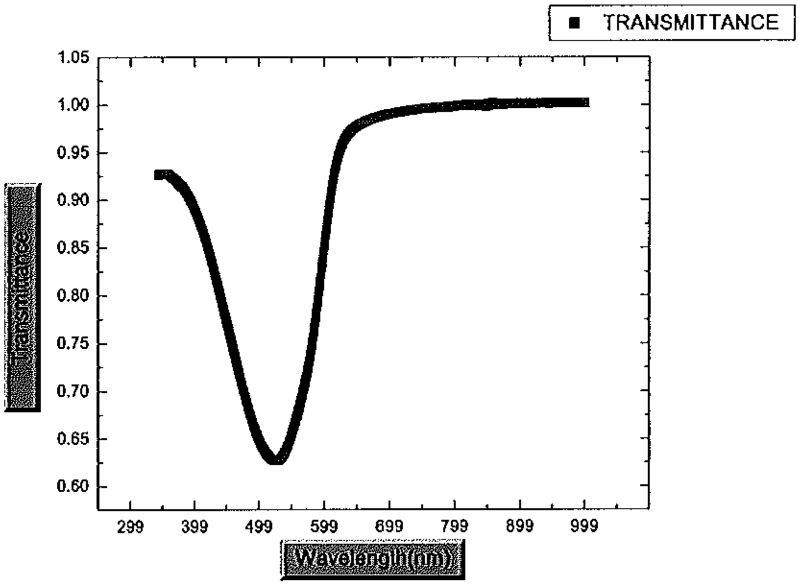

Figure 3.1: Wave length versus transmittance measurment

that the sample has good glass character.

3.2 Experimental Procedure

Reflection ellipsometric data measurements for polymers are conducted at an angle of incidence between 60^0 and 70^0 [2]. The values of α and β are determined from curve fitting for rotating analyzer technique where as the ellipsometric parameters ψ and Δ are calculated from α and β. The relations are given in section (2.2)

For Static Photometric ellipsometer technique ψ and Δ are directly calculated from the intensity measured at the detector for three polarizer angels as explained in section (2.3) of Eqs. (2.3.8) and (2.3.9). Schematic representation of the experimental set up is as shown below in figure 3.2 which consists of laser source (He-Ne laser model 1125p/Diode laser model LDC 01 SER.No. 6150-139), two polarizers (one polarizer and one analyzer), chopper model SR 540, sample, photo-conducting detector and Lock-In amplifier made of Stanford Research Group MODEL SR830.

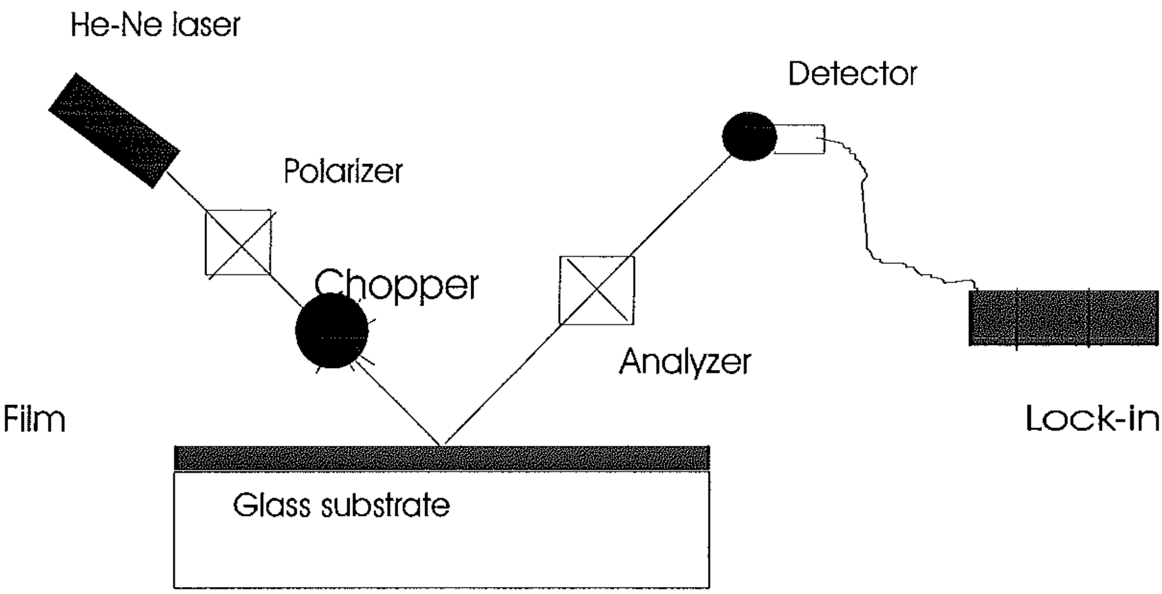

Figure 3.2: Graph of experimental set up.

3.3 Data and Data Analysis

The table 1. Intensity versus analyzer angle at different angle of incidences.

A^0	I at$\theta = 60^0$	I at$\theta = 61^0$	I at$\theta = 63^0$	I at$\theta = 65^0$	I at$\theta = 67^0$	I at$\theta = 70^0$
0	0.00462	0.00384	0.00345	0.00389	0.00494	0.00551
5	0.00465	0.00383	0.00348	0.00393	0.00487	0.00542
10	0.00464	0.00379	0.00338	0.00393	0.00477	0.00524
15	0.00461	0.00375	0.00348	0.00389	0.00464	0.00504
20	0.00453	0.00365	0.00342	0.00382	0.00444	0.00483
25	0.0044	0.0035	0.00336	0.00352	0.00428	0.00457
30	0.00127	0.00335	0.00326	0.00333	0.00402	0.0043
35	0.00416	0.00317	0.00316	0.00333	0.00376	0.00394
40	0.00397	0.00289	0.00302	0.00327	0.00342	0.00361

continued....

A^0	I at$\theta = 60^0$	I at $\theta = 61^0$	I at $\theta = 63^0$	I at $\theta = 65^0$	I at$\theta = 67^0$	I at$\theta = 70^0$
45	0.00384	0.00257	0.00284	0.0031	0.00314	0.00316
50	0.0036	0.00223	0.00265	0.00284	0.00278	0.00276
55	0.00333	0.0019	0.00248	0.00265	0.00238	0.00228
60	0.00298	0.00162	0.00223	0.00237	0.0019	0.00181
65	0.00269	0.00132	0.00194	0.00202	0.00151	0.00119
70	0.00238	0.00102	0.00168	0.00171	0.00109	8.88E-04
75	0.00199	0.73E-04	0.0014	0.00135	6.76E-04	8.70E-04
80	0.00169	5.43E-04	0.00106	0.00109	5.29E-04	8.64E-04
85	0.00146	2.96E-04	7.29E-04	6.30E-04	6.86E-04	0.00141
90	0.00134	1.72E-04	4.20E-04	4.12E-04	0.00113	0.00186
95	0.00141	2.46E-04	2.13E-04	3.17E-04	0.00165	0.00236
100	0.00163	4.62E-04	9.22E-05	4.20E-04	0.00202	0.00289
105	0.00206	7.73E-04	1.46E-04	8.35E-04	0.00245	0.00326
110	0.00241	0.00112	3.57E-04	0.00114	0.00292	0.00358
115	0.00266	0.00147	6.71E-04	0.00155	0.0032	0.00384
120	0.00296	0.0018	9.92E-04	0.00207	0.00353	0.0042
125	0.0032	0.00213	0.00126	0.00219	0.00382	0.00445
130	0.00348	0.0024	0.00153	0.00257	0.00394	0.00468
135	0.00372	0.00267	0.00182	0.00289	0.00416	0.00489
140	0.00389	0.00292	0.00208	0.00316	0.00423	0.00507
145	0.00411	0.00311	0.00226	0.00342	0.00454	0.00518
150	0.00424	0.00332	0.0025	0.00361	0.00473	0.00529
155	0.00436	0.00348	0.00265	0.00379	0.00487	0.00536
160	0.00449	0.0036	0.00278	0.00397	0.00496	0.0054
165	0.00456	0.0037	0.00307	0.0041	0.005	0.00542
170	0.00462	0.00375	0.00301	0.00419	0.00503	0.00539
175	0.00465	0.00379	0.00306	0.00425	0.00501	0.00534

continued......

A^0	I at $\theta = 60^0$	I at $\theta = 61^0$	I at $\theta = 63^0$	I at $\theta = 65^0$	I at$\theta = 67^0$	I at $\theta = 70^0$
180	0.00466	0.00379	0.00312	0.0043	0.00496	0.00524
185	0.00464	0.00377	0.00319	0.00433	0.00484	0.00514
190	0.00461	0.00376	0.00316	0.00432	0.00472	0.005
195	0.00453	0.0037	0.00318	0.00426	0.00456	0.00479
200	0.00446	0.0036	0.0032	0.00419	0.0044	0.00453
205	0.00436	0.00346	0.0032	0.00407	0.00424	0.0043
210	0.00424	0.00332	0.00317	0.00398	0.00402	0.00408
215	0.00406	0.00314	0.00308	0.00383	0.00378	0.00375
220	0.00387	0.00295	0.00298	0.00364	0.00346	0.00336
225	0.00365	0.00272	0.00285	0.0034	0.00308	0.00292
230	0.00339	0.00251	0.00267	0.00314	0.00283	0.00255
235	0.00314	0.00224	0.00251	0.00287	0.00238	0.00214
240	0.00287	0.00193	0.00221	0.0025	0.00201	0.00165
245	0.00251	0.0016	0.00197	0.0022	0.00149	0.00124
250	0.00215	0.00126	0.0018	0.0019	0.00104	8.24E-04
255	0.00181	9.06E-04	0.00146	0.00157	6.35E-04	6.10E-04
260	0.00159	5.86E-04	0.00116	0.00123	4.97E-04	9.49E-04
265	0.00132	2.99E-04	8.12E-04	8.18E-04	6.66E-04	0.00131
270	0.00124	1.82E-04	4.80E-04	4.67E-04	8.70E-04	0.00177
275	0.00127	2.19E-04	2.37E-04	3.50E-04	0.00145	0.00243
280	0.00144	4.33E-04	1.14E-04	3.96E-04	0.00194	0.0028
285	0.00175	7.40E-04	1.59E-04	6.81E-04	0.00235	0.00325
290	0.00212	0.00112	3.80E-04	9.12E-04	0.00271	0.00365
295	0.0025	0.00147	6.35E-04	0.00126	0.00308	0.00402
300	0.00283	0.00182	0.00106	0.00164	0.00342	0.00434
305	0.00316	0.00213	0.00136	0.00189	0.00372	0.00461
310	0.00339	0.00244	0.00168	0.00216	0.00402	0.0049

continued......

A^0	I at $\theta = 60^0$	I at $\theta = 61^0$	I at $\theta = 63^0$	I at $\theta = 65^0$	I at$\theta = 67^0$	I at $\theta = 70^0$
315	0.0036	0.00269	0.00193	0.00244	0.00426	0.00507
320	0.00383	0.00294	0.00221	0.00266	0.00449	0.00523
325	0.00402	0.00314	0.00246	0.00295	0.00465	0.0054
330	0.00416	0.00332	0.00267	0.00312	0.00479	0.00551
335	0.0043	0.00348	0.00286	0.00328	0.00487	0.00557
340	0.00444	0.00361	0.00304	0.00339	0.00494	0.00561
345	0.00453	0.00371	0.00316	0.00352	0.00498	0.00562
350	0.0046	0.00378	0.00327	0.00361	0.00496	0.0056
355	0.00465	0.00382	0.00338	0.00372	0.00496	0.00552
360	0.00468	0.00384	0.00342	0.00378	0.00491	0.00548

Intensity versus analyzer angle is plotted and the data is analyzed fitting to the Eq. (2.2.25) which is a model equation developed for calculating the constants α and β.

The graph in figure 3.3 shows that the intensity versus analyzer angle plotted at an angle of incidence of $\theta = 60^0$. The dotted curve indicates the experimental results while the line curve indicates the fitting.

Table 2. For different angle of incidences, the constants α and β obtained from curve fitting, the calculated values of $\tan\psi$, $\cos\Delta$ and n,for a laser light of wavelength $\lambda = 632.8$ nm Table 2.

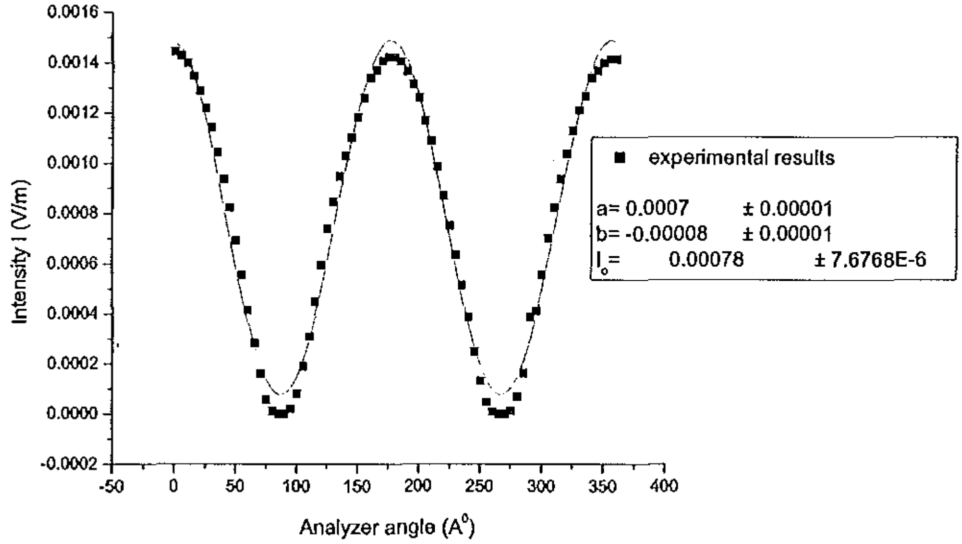

Figure 3.3: Intensity versus analyzer angle.

θ_0	α	β	$\tan\psi$	$\cos\Delta$	n
60	0.0015	-0.00004	1.7346	-0.00004	1.7322
61	0.0017	-7.1555*10^{-7}	1.0017	-7.1555*10^{-7}	1.8041
63	0.00137	0.00056	1.0014	0.00056	1.9609
65	0.00165	0.00033	1.0017	0.00033	2.1433
67	0.00186	-0.00068	1.0019	-0.00003	2.3559
70	0.00181	-0.00112	1.0018	-0.00112	2.7529

Table 3, shows the refractive index of the polymer using the equations developed for Static Photometric ellipsometer at a wavelength of 632.8 nm.

Table 3.

p^0	θ^0	$I_{D1} at$-45^0	$I_{D2} at 0^0$	$I_{D3} at 45^0$	n
45	60	0.0384	0.0462	0.0360	1.816
45	61	0.0257	0.0384	0.0269	1.693
45	63	0.0449	0.0543	0.0472	1.870
45	65	0.0450	0.0573	0.0508	1.900
45	67	0.0314	0.0494	0.0426	1.708
45	70	0.0316	0.0551	0.0507	1.558

Table 4, shows the values of constants α and β obtained from curve fitting at different angles of incidence along with the calculated values of n, $\tan\psi$ and $\cos\Delta$ for wavelength of $\lambda = 808.4$ nm. Table 4.

θ_0	α	β	$\tan\psi$	$\cos\Delta$	n
60	0.00114	0.00074	1.0011	0.00074	1.7301
63	0.00042	0.00035	1.0004	0.00035	1.9615
65	0.00035	0.00024	1.0004	0.00024	2.1437
67	0.00026	0.00029	1.0003	0.00029	2.3547
70	0.00025	0.00042	1.0003	0.00042	2.7454

Table 5 shows the calculated refractive index of the thin film polymer sample using the equations of static photometric ellipsometer for a diode laser at a wavelength of 808.4 nm for different angles of incidence between 60^0 and 70^0. Table 5.