Development of a Technique to Determine the Temperature Dependence of the Refractive Index of Carbonaceous Particulates.

Barry James Stagg

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Development of a technique to determine the temperature dependence of the refractive index of carbonaceous particulates

Stagg, Barry James, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1992

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DEVELOPMENT OF A TECHNIQUE TO DETERMINE THE TEMPERATURE DEPENDENCE OF THE REFRACTIVE INDEX OF CARBONACEOUS PARTICULATES

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Mechanical Engineering

by

Barry James Stagg
B.S.M.E., Louisiana State University, 1986
May, 1992
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**Roman Letters**

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<td>$a_0, \tilde{a}_n, \tilde{b}_n$</td>
<td>Fourier coefficients</td>
</tr>
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<td>$a_n, b_n$</td>
<td>normalized Fourier coefficients</td>
</tr>
<tr>
<td>$A$</td>
<td>analyzer azimuth</td>
</tr>
<tr>
<td>$A_N$</td>
<td>sensitivity</td>
</tr>
<tr>
<td>$\mathbf{B}$</td>
<td>magnetic field vector</td>
</tr>
<tr>
<td>$\mathbf{E}$</td>
<td>electric field vector</td>
</tr>
<tr>
<td>$\mathbf{E}_{x,y}$</td>
<td>Jones vector</td>
</tr>
<tr>
<td>$e$</td>
<td>electron charge (Chapter 1); extinction ratio of polarizer</td>
</tr>
<tr>
<td>$g_b$</td>
<td>damping constant of bound electrons</td>
</tr>
<tr>
<td>$g_f$</td>
<td>damping constant of free electrons</td>
</tr>
<tr>
<td>$I$</td>
<td>intensity of light</td>
</tr>
<tr>
<td>$i$</td>
<td>$\sqrt{-1}$</td>
</tr>
<tr>
<td>$[J]$</td>
<td>coherency matrix</td>
</tr>
<tr>
<td>$J_{xz}, J_{yz}, J_{yx}, J_{yy}$</td>
<td>elements of the coherency matrix</td>
</tr>
<tr>
<td>$k$</td>
<td>absorptive index, $k = \text{Im}(\tilde{n})$</td>
</tr>
<tr>
<td>$k_A$</td>
<td>first principal transmittance of the analyzer</td>
</tr>
<tr>
<td>$k_P$</td>
<td>first principal transmittance of the polarizer</td>
</tr>
<tr>
<td>$k_1$</td>
<td>first principal transmittance of a polarizing component</td>
</tr>
<tr>
<td>$k_2$</td>
<td>second principal transmittance of a polarizing component</td>
</tr>
<tr>
<td>$\tilde{m}$</td>
<td>complex refractive index, $\tilde{m} = n - ik$</td>
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n \text{ refractive index, } n = \text{Re}(\bar{m})
n_b \text{ number density of bound electrons}
n_f \text{ number density of free electrons}
P \text{ polarizer azimuth; degree of polarization (Chapter 2)}
\bar{r}_p \text{ parallel component of electric field reflectivity}
\bar{r}_s \text{ perpendicular component of electric field reflectivity}
R_{\|} \text{ parallel component of intensity reflectivity}
R_{\perp} \text{ perpendicular component of intensity reflectivity}
\bar{S} \text{ Stokes vector}
s_0, s_1, s_2, s_3 \text{ parameters of the Stokes vector}
S_N \text{ adjusted standard error}
SI \text{ specularity index}
V \text{ Verdet constant}

\textbf{Greek Letters}
\alpha_1, \beta_1 \text{ birefringence parameters of entrance window}
\alpha_2, \beta_2 \text{ birefringence parameters of exit window}
\alpha \text{ correlation distance of a random roughness distribution}
\Delta \text{ second ellipsometric parameter}
\epsilon_0 \text{ permittivity of free space}
\epsilon \text{ complex dielectric function, } \epsilon = (n - ik)^2
\delta \text{ phase of electric field vector component}
\delta A \text{ analyzer offset}
\delta P \text{ polarizer offset}
\lambda \text{ wavelength of radiation}
\Delta \lambda \text{ spectral bandwidth of radiation}
\rho e^{i\Delta} \text{ complex ellipsometric parameter}
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<tr>
<td>$\rho$</td>
<td>first ellipsometric parameter; surface roughness factor (Chapter 4); density (Chapter 8)</td>
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<tr>
<td>$\theta$</td>
<td>angle of incidence</td>
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<tr>
<td>$\sigma$</td>
<td>root mean square roughness of a random roughness distribution (Chapter 4); standard error (Chapter 6)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>frequency of radiation</td>
</tr>
<tr>
<td>$\omega_b$</td>
<td>natural frequency of bound electrons</td>
</tr>
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Abstract

The complex refractive index of carbonaceous particulates is an important quantity in many areas of combustion research and practical applications. This property characterizes the radiative transport in luminous flames and plays a key role in the interpretation of conventional light scattering measurements. The purpose of the present study is to develop a technique which will allow the experimental determination of the temperature dependence of the refractive indices of carbonaceous materials and provide a predictive model for the variation of the indices.

A high temperature ellipsometer system is developed that allows measurements of the intensity of polarized light reflected from the surface of a bulk sample enclosed in a temperature controlled environment. Measurements are possible in the range of angles of incidence 40° to 50° and in the temperature range 25°C to 2300°C under rough vacuum and inert conditions. The reflected light intensities are measured with respect to the variation of the angular polarization state and the data are reduced using Fourier analysis. The optical components of the experimental system are arranged to form a PSA ellipsometer. The effects of cell window birefringence, sample surface roughness and polarizer leakage on
ellipsometry measurements are discussed. In addition, the role of the angle of incidence and the analyzer azimuth on numerical precision are assessed.

The refractive indices of three carbonaceous samples (amorphous carbon, pyrolytic graphite and flame soot) are determined over the temperature range 25–600°C and the spectral range 400–700 nm. It was seen that for all three of these materials, the measured refractive index shows insignificant temperature dependence. These results differ by 30 percent or more from the predictions of the Drude–Lorentz dispersion model, which has been used extensively to predict the variation of the optical properties of carbonaceous particulates. A new set of dispersion constants is developed from the inferred refractive indices that accurately predict the indices in the temperature range 25–600°C and in the wavelength range 400–700 nm.
Chapter 1

Introduction

The complex refractive index \((n - ik)\) of carbonaceous particulates such as soot is an important quantity in many areas of combustion research. This property characterizes the radiative transport in luminous flames and plays a key role in the interpretation of conventional light scattering measurements. Although the refractive index of soot has been widely studied, very little is known about its variation with temperature. Data for the refractive indices of soot in both visible and infrared wavelengths have been obtained by a number of investigators [1-13]. However, the substantial differences between the existing values of the indices make the choice of the appropriate refractive index difficult. The use of various reasonable values of the index [14] can lead to number densities that differ by a factor of five or more. It has been pointed out that the mass growth rates of soot may differ by 100 percent when different refractive indices are employed in the data analysis [15].
Previous measurements of soot refractive indices may be divided into two categories: \textit{in-situ} \cite{1,4,7-8,11-13}, where the measurements are performed under flame conditions, and \textit{ex-situ} \cite{2-3,5-6,9-10} where the soot is extracted from the flame prior to the measurement. The advantages and disadvantages of each technique have been assessed by many investigators \cite{9-13,16-18}. However, none of these studies have actually dealt with the temperature dependence of the refractive index of soot or other carbonaceous materials.

\textit{Ex-situ} techniques utilize two basic methods. In the first method, used by Dalzell and Sarofim \cite{3}, Tomasseli \textit{et al.} \cite{6}, Felske \textit{et al.} \cite{9}, and Batten \cite{10}, the soot particles were collected with sampling probes or water cooled plates and then compressed into smooth pellets. The complex refractive index is then found by measuring the intensity of polarized light reflected from the sample surface under room temperature conditions. In the second \textit{ex-situ} method, used by Janzen \cite{16}, the soot particles are dispersed in a transparent medium of known refractive index and then the spectral transmittance of the mixture is measured. A fundamental problem that arises with respect to all \textit{ex-situ} techniques is that the particle morphology and temperature is not representative of the soot particles under flame conditions.

The \textit{in-situ} techniques employ a combination of light scattering and transmittance measurements in a laboratory flame system. The main drawback of the \textit{in-situ} technique lies in the fact that the actual particle shape is not precisely
known under flame conditions. Specifically, as noted by various investigators (see for example [19–27]), subsequent to their formation, the soot particles agglomerate into arbitrary structures such as chains and/or clusters. Another drawback of the in-situ technique in determining refractive index is the necessity of knowing the size and number density of the soot particles present in the flame. Furthermore, at long wavelengths transmittance measurements are difficult to obtain and the experimental uncertainty must be as low as possible [28].

The temperature dependence of radiative properties of various types of carbons and graphites have been studied by other investigators. Plunkett and Kingery [29] measured the emissivities of carbon, graphite, and pyrolytic graphite with different surface characteristics over the temperature range 850–1800°C. Results for graphite show that for a highly polished surface produced by burnishing, the spectral emissivity is almost independent of temperature, while the integrated emissivity value shows a positive temperature dependence. Carbon, on the other hand, shows no temperature dependence for emissivity but the emissivity changes with surface treatment. The differences in the temperature dependence appear to be related to the anisotropic optical properties of graphite. The emissivity of carbon and graphite is a poorly understood property, in spite of the numerous measurements made. Autio and Scala [30] measured the spectral emissivity of pyrolytic and polycrystalline graphite in the temperature range 844–1174°C and
in the wavelength range 2.5–13 μm. They found no temperature dependence for
the emissivity in this range of temperature and wavelength.

The Drude–Lorentz dispersion model has been utilized by several investiga
tors [8,31–32] to predict the temperature and wavelength dependence of the
refractive indices of soot particles. The Drude–Lorentz model considers the solid
to be an assembly of oscillators (electrons) which are set into forced vibration by
the incident radiation. Each oscillator has an associated damping constant and
a resonant frequency. The free (conduction) electrons have a resonant frequency
of zero. Soot has been modelled to possess the same optical transitions as those
of graphite, meaning that its electrons have the same resonant frequencies as
graphite. Graphite has three bound electrons and one loosely bound electron.
Since the transition band of one of the bound electrons occurs well below the
ultraviolet, an account of the optical properties in the visible and infrared can be
obtained by considering only two bound electrons, for which optical transitions
occur at 0.26 and 1.5 μm.

The real and imaginary parts of the index \((n,k)\) may be expressed in terms
of the number densities of the bound and free electrons \((n_b, n_f)\), the natural
frequencies of the bound electrons \((\omega_b)\), and damping constants of the bound
and free electrons \((\gamma_b, \gamma_f)\) through the dispersion equations [8]

\[
n^2 - k^2 = 1 + \frac{e^2}{m\epsilon_0} \sum_{j=1}^{2} \frac{n_b \omega^2 - \omega^2}{\omega^2 \omega^2 + \omega^2 \gamma_b} - \left(\frac{e^2}{m^* \epsilon_0}\right) \frac{n_f}{\omega^2 + \gamma_f^2} \tag{1.1}
\]
The parameters \( m \) and \( m^* \) represent the masses of the bound and free electrons respectively, \( e \) is the charge on an electron, \( \epsilon_0 \) is the permittivity of free space and \( \omega \) is the frequency of the incident radiation.

The dispersion constants utilized for the forward calculations of this study are those found by Charalampopoulos and Chang [13] and are shown in Table 1.1.

### Table 1.1: Dispersion constants from Charalampopoulos and Chang [13].

<table>
<thead>
<tr>
<th>Type of Electron</th>
<th>Electron number density ( m^{-3} )</th>
<th>Frequency ( \omega \times 10^{-15} \text{sec}^{-1} )</th>
<th>Damping constant ( g \times 10^{-15} \text{sec}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free:</td>
<td>( 4.82 \times 10^{28} )</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>Bound 1:</td>
<td>( 3.88 \times 10^{27} )</td>
<td>1.25</td>
<td>6.1</td>
</tr>
<tr>
<td>Bound 2:</td>
<td>( 4.26 \times 10^{28} )</td>
<td>7.25</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Previous investigators have utilized the Drude–Lorentz model to predict the temperature dependence of the refractive index of soot by assuming that the damping constants of the free and bound electrons change with temperature. Lee and Tien [8] and Charalampopoulos et al. [31] assumed that the damping constants of the electrons were proportional to the square root of temperature. With this assumption, Charalampopoulos et al. [31] calculated the refractive
index in the temperature range 300 K to 1800 K. It was shown that the real part \((n)\) of the complex refractive index is relatively insensitive to temperature change. Specifically, it was found that the real part \((n)\) changes by less than five percent, whereas the imaginary part \((k)\) of the refractive index may change by more than 50 percent when the temperature varies in this temperature range. Howarth et al. [32] assumed that the damping constants of the electrons were directly proportional to temperature and also assumed that the number density of free electrons increased with temperature. The assumption that the damping constants of the electrons are directly proportional to temperature is the extreme case corresponding to a perfect crystal and should therefore predict the maximum effect temperature can have on the refractive index. In this case, the real part of the refractive index was seen to change by as much as 20 percent as the temperature was varied from 300 K to 2000 K and the imaginary part of the refractive index was seen to vary as much as 300 percent for the same temperature change. Since most carbonaceous particulates occurring in combustion systems are not perfect crystals, Howarth et al. [32] point out that their predicted temperature effects are too large.

As previously described, the Drude–Lorentz dispersion model has been used to predict the wavelength and temperature dependence of the complex refractive index of flame soot. However, the accuracy of these predictions can be questioned. Although the Drude–Lorentz model has logical foundations, the model can only
be considered empirical when applied to a material which is not a perfect crystal. Also, the temperature dependence of the dispersion model parameters, such as electron damping constants and oscillator strengths, is not precisely known.

Ideally, the temperature dependence of the index of refraction of combustion generated particulates should be evaluated under flame conditions. Nevertheless, as was mentioned earlier, the in-situ technique presents problems and uncertainties which hinder the accurate determination of refractive index. In addition and most importantly, accurate temperature control under flame conditions is a difficult task. Therefore, as a first step, an ex-situ study for this type of investigation is more suitable.

The purpose of the present study is to develop an experimental facility and a measurement technique which will allow the experimental determination of the temperature dependence of the refractive indices of carbonaceous materials. This is accomplished by measuring the intensity of polarized light reflected from the surface of a bulk sample contained in a temperature controlled environment. The optical technique utilized is known as photometric ellipsometry. Two major techniques exist for measuring the refractive index of materials in bulk. These two techniques are known as reflectometry and ellipsometry. Reflectometry involves the measurement of the intensity of light reflected from a sample in order to determine the reflectivities. The reflected intensity may be measured in the plane of polarization parallel ($R_\parallel$) or perpendicular ($R_\perp$) to the plane of incidence
and at one or more angles of incidence. Ellipsometry is based on the principle that linearly polarized light incident upon a sample is reflected as elliptically polarized light and the characteristics of this ellipse are dependent upon the optical properties of the sample. The principles behind ellipsometry have been known from the time of Drude [33]. Both techniques have been used extensively to determine the refractive indices of absorbing samples. Ellipsometry is also widely used in the study of thin films [34–38], such as oxidation layers on metallic substrates [38] and oxide layers on semiconductors [34–36].

In both ellipsometry and reflectometry, two independent quantities must be measured at any given wavelength in order to infer the real (\(n\)) and imaginary (\(k\)) parts of the complex refractive index. Both techniques are suitable for determining the optical properties of materials when measurements are taken from a bare substrate at a single angle of incidence. The exception occurs when reflectometry is used at an angle of incidence of 45°. At 45° angle of incidence, the reflection coefficients parallel \(R_{\parallel}\) and perpendicular \(R_{\perp}\) to the plane of incidence are no longer independent quantities, but are related by the expression \(\left[R_{\perp}^2/R_{\parallel}\right]_{\theta=45^\circ} = 1.0\). This relation also necessitates that the surface of the sample is catoptrically flat [39]. Therefore, ellipsometry is the preferred technique to determine the complex refractive index of a material when the measurements are to be carried out at 45°. At this point, it should be noted that reflection measurements at 45° are useful in order to assess the optical quality of the surface by
measuring the specularity index, $\left[ R_2^2 / R_1^1 \right]_{\theta=45^\circ}$ [40]. It is also noted that reflection measurements are useful for determining the optical properties of materials in the liquid phase. This will be the case, for example, in optical studies of liquid ceramics, such as Al$_2$O$_3$, where containment of the sample in conventional type cells suitable for transmission measurements is not possible. This is due mainly to the lack of materials with high melting points and appropriate optical characteristics in both the visible and infrared wavelengths. In these cases, a high temperature unit with resistance heating capabilities and optical access from the sides is better suited. Nevertheless, in order to accomplish sufficiently high temperatures, the size of the optical ports needs to be small. This results in a limited angular range over which measurements can be carried out. Since the reflection technique is relatively insensitive for reliable inference of optical properties when the angular range is small, especially in the vicinity of 45°, the ellipsometry technique is better suited.

In this particular study, the behavior of three different carbonaceous samples will be investigated in the wavelength range 400–700 nm. These three samples are amorphous carbon, pyrolytic graphite, and flame soot. The scope of this work includes a presentation of the theory describing the interaction of electromagnetic waves with matter. The equations used to invert the data are derived utilizing this theory, and an assessment of the influence of surface roughness on polarized reflection measurements is also presented. A sensitivity analysis of
the data inversion scheme is presented, followed by a description of the experimental facility. The procedure used to align the optical system is given and the experimental system is tested by performing measurements on a sample of known optical properties. Finally, the results are presented, which include the experimentally determined birefringence parameters and also the experimentally determined refractive indices of the three carbonaceous samples. A discussion of these results is presented and recommendations for future work are made. Also listed with these recommendations are suggestions for improving the experimental apparatus and measurement technique.
Chapter 2

Theory

As stated in Chapter 1, the purpose of this study is to determine the temperature dependence of the refractive index of carbonaceous materials. Because the refractive index is found from the interaction of polarized light with the surface of the sample, a brief presentation of the theory of polarized light is in order. Specifically, in this chapter the mathematical methods of characterizing the polarization of light beams through the use of the Jones vector and the Stokes vector will be discussed. The manner in which Jones and Mueller calculus can be used to describe the change of polarization of a light beam as it interacts with an optical element is also discussed. In addition, a brief presentation of the coherency matrix formulation is given as an alternative method for describing beam polarization characteristics. Finally, the specifics of the application of the Mueller calculus to the present study is discussed and a description of the reflection of light from a surface is presented.
2.1 Description of Polarization

All electromagnetic waves are transverse in nature, and therefore exhibit polarization. The transverse nature of electromagnetic waves is characterized by the electric-field strength vector, \( \vec{E} \), and the magnetic field strength vector, \( \vec{B} \). It can be shown [33] that both of these vectors are perpendicular to the direction of propagation and are also perpendicular to each other, with the direction of propagation being parallel to the vector \( \vec{k} = \vec{E} \times \vec{B} \). Because the electric field strength vector and the magnetic strength field vector are related by Maxwell's field equations, the polarization of an electromagnetic wave can be characterized by describing the polarization of either \( \vec{E} \) or \( \vec{B} \). Traditionally, \( \vec{E} \) has been chosen to define the polarization state of electromagnetic waves. This choice comes about from the fact that the force exerted on a charged particle by the electric field of a light wave is much greater than the force exerted by the magnetic field of the same light wave (provided the speed of the particle does not approach the speed of light). Therefore, the polarization of light is defined by the behavior of the electric field vector, \( \vec{E} \).

A Fourier analysis of the time variation of \( \vec{E} \) of a light beam yields, in the most general case, an infinite range of frequencies. A light beam is said to be monochromatic if only one discrete frequency is present and is said to be polychromatic if a range of frequencies exists. The beam is characterized as quasi-monochromatic if its frequency distribution is described by a narrow spectral line.
of very small but finite width. The time variation of the electric field vector of a perfectly monochromatic wave is exactly sinusoidal, with a frequency \( \omega = 2\pi c/\lambda \), where \( c \) is the speed of light and \( \lambda \) is the wavelength. Therefore, a wave at a particular frequency can be described fully by the phase and amplitude of that wave.

As mentioned earlier, the electric field vibrations are in a direction perpendicular to the direction of light propagation. Therefore, if a Cartesian coordinate system is chosen such that the \( \vec{z} \) axis is parallel to the direction of propagation, the electric field vector will have components in only the \( \vec{x} \) and \( \vec{y} \) directions. Each component of the electric field vector in the \( \vec{x} \) and \( \vec{y} \) direction will have an associated amplitude and phase, and, in complex notation, can be written as

\[
\tilde{E}_x = E_x e^{i\delta_x} \quad (2.1)
\]

and

\[
\tilde{E}_y = E_y e^{i\delta_y} \quad (2.2)
\]

where \( i = \sqrt{-1} \). This description of polarization can be arranged in the form of a column vector as

\[
\tilde{E}_{x,y} = \begin{bmatrix} \tilde{E}_x \\ \tilde{E}_y \end{bmatrix} = \begin{bmatrix} E_x e^{i\delta_x} \\ E_y e^{i\delta_y} \end{bmatrix} , \quad (2.3)
\]

where \( \tilde{E}_{x,y} \) is called the Jones vector of a wave [33,41], and the \( \sim \) symbol signifies a complex variable. Because the point of reference (origin of coordinate system) is arbitrary, the absolute phase components, \( \delta_x \) and \( \delta_y \), are also somewhat
arbitrary, and only the phase difference, \( \delta_y - \delta_x \) is important. The intensity of a beam is given as the sum of the squares of the vector amplitudes as

\[
I = E_x^2 + E_y^2 .
\]

(2.4)

Equivalently, the intensity may be written as the dot product of the Jones vector with its complex conjugate as

\[
I = \bar{E}_{x,y} \cdot \bar{E}_{x,y} ,
\]

(2.5)

where \( \bar{E}_{x,y} \) represents the complex conjugate of \( E_{x,y} \).

The Jones vector is only one of many tools used to describe polarization. Another useful tool is the Stokes vector, discovered by George G. Stokes [42]. The Stokes vector is a set of four real parameters which describe the intensity and polarization of a light beam. The Stokes vector is given in column form as

\[
\vec{S} = \begin{bmatrix}
  s_0 \\
  s_1 \\
  s_2 \\
  s_3
\end{bmatrix},
\]

(2.6)

where the Stokes parameters are given in terms of the wave amplitudes \( (E_x, E_y) \) and phases \( (\delta_x, \delta_y) \) as [43]

\[
s_0 = E_x^2 + E_y^2 ,
\]

\[
s_1 = E_x^2 - E_y^2 ,
\]

\[
s_2 = 2E_x E_y \cos (\delta_y - \delta_x)
\]

(2.7)

and

\[
s_3 = 2E_x E_y \sin (\delta_y - \delta_x) .
\]
The parameter \( s_0 \) represents the beam intensity, whereas \( s_1 \) indicates the preference for horizontal or vertical polarization. The parameter \( s_2 \) indicates the preference for \(+45^\circ\) or \(-45^\circ\) linear polarization and \( s_3 \) indicates a preference for circular polarization [41]. The Stokes and Jones vectors are column vectors, but are commonly written as row vectors to save space (i.e. \( \vec{S} = \{s_0, s_1, s_2, s_3\} \)). The vectors are then enclosed by curly brackets as a reminder that Jones and Stokes vectors are actually column vectors. When the Stokes vector parameters are normalized by the intensity (\( s_0 \)), the magnitude of \( s_1, s_2, \) and \( s_3 \) take on values between negative one and positive one. Therefore, the normalized Stokes vector of a vertically polarized beam will have \( s_1 = -1, s_2 = s_3 = 0 \) and a horizontally polarized beam will have \( s_1 = +1, s_2 = s_3 = 0 \). The Jones vector can also be normalized with respect to intensity, with the intensity given by equations (2.4) or (2.5). The normalized Stokes and Jones vectors of some common beam polarizations are shown in Table 2.1 [41].

The Jones vector of equation (2.3) is a linear superposition of the orthonormal Jones vectors, \( \hat{\varepsilon}_x \) and \( \hat{\varepsilon}_y \), given by

\[
\vec{E}_{x,y} = \vec{E}_x \hat{\varepsilon}_x + \vec{E}_y \hat{\varepsilon}_y ,
\]

where \( \hat{\varepsilon}_x \) and \( \hat{\varepsilon}_y \) play the role of basis vectors [33,44]. Different basis vectors may be more suitable for certain problems and the Jones and Stokes vectors can be described in terms of such basis vectors. Of particular interest are the basis vectors \( \hat{\varepsilon}_l \) and \( \hat{\varepsilon}_r \) which correspond to left and right circular polarizations [33,44].
Table 2.1: Normalized Stokes and Jones vectors.

<table>
<thead>
<tr>
<th>Type of Polarization</th>
<th>Normalized Stokes Vector</th>
<th>Normalized Jones Vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>horizontal linear</td>
<td>{1,1,0,0}</td>
<td>{1,0}</td>
</tr>
<tr>
<td>vertical linear</td>
<td>{1,-1,0,0}</td>
<td>{0,1}</td>
</tr>
<tr>
<td>+45° linear</td>
<td>{1,0,1,0}</td>
<td>\sqrt{2}{1,1}</td>
</tr>
<tr>
<td>-45° linear</td>
<td>{1,0,-1,0}</td>
<td>\sqrt{2}{1,-1}</td>
</tr>
<tr>
<td>general linear</td>
<td>{1,\cos(2\alpha),\sin(2\alpha),0}</td>
<td>{\cos(\alpha),\sin(\alpha)}</td>
</tr>
<tr>
<td>right circular</td>
<td>{1,0,0,1}</td>
<td>\sqrt{2}{-i,1}</td>
</tr>
<tr>
<td>left circular</td>
<td>{1,0,0,-1}</td>
<td>\sqrt{2}{i,1}</td>
</tr>
<tr>
<td>unpolarized</td>
<td>{1,0,0,0}</td>
<td>none</td>
</tr>
</tbody>
</table>

In this case, the Jones vector is given as \[33\]

\[
\vec{E}_{x,y} = \vec{E}_i \hat{\varepsilon}_i + \vec{E}_r \hat{\varepsilon}_r ,
\]  

where \(\hat{\varepsilon}_i\) and \(\hat{\varepsilon}_r\) are given as \(\hat{\varepsilon}_i = \frac{1}{\sqrt{2}}\{1,-i\}\) and \(\hat{\varepsilon}_r = \frac{1}{\sqrt{2}}\{1,i\}\). The basis Jones vector \(\hat{\varepsilon}_i\) represents an electric vector of unit length that rotates counter-clockwise around the \(z\) axis and similarly, \(\hat{\varepsilon}_r\) represents an electric vector of unit length that rotates clockwise around the \(z\) axis. Using the definitions of \(\hat{\varepsilon}_i\) and \(\hat{\varepsilon}_r\), equation (2.9) can be written in the form

\[
\begin{bmatrix} \vec{E}_x \\ \vec{E}_y \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -i & i \end{bmatrix} \begin{bmatrix} \vec{E}_i \\ \vec{E}_r \end{bmatrix}
\]  

(2.10)

or

\[
\vec{E}_{x,y} = [F] \vec{E}_{i,r} ,
\]  

(2.11)
where \([F]\) is the transformation matrix that links the circular basis Jones vector to the Cartesian basis Jones vector.

The Stokes vector can also be described in terms of the circular basis vectors as [43]

\[
\begin{align*}
S_0 &= E_l^2 + E_r^2, \\
S_1 &= 2E_lE_r \cos(\delta_l - \delta_r), \\
S_2 &= 2E_lE_r \sin(\delta_l - \delta_r) \\
S_3 &= E_l^2 - E_r^2.
\end{align*}
\]

(2.12)

and

For purposes of this study, only the Cartesian basis vectors will be utilized. Therefore, the Jones and Stokes vectors encountered from here on will be with respect to the Cartesian basis vectors and the subscript on the Jones vector will be eliminated. The four Stokes parameters are not independent since they depend on only three quantities \(E_x, E_y, \) and \(\delta_y - \delta_x\). They satisfy the relation

\[
S_0^2 = S_1^2 + S_2^2 + S_3^2.
\]

(2.13)

Up to this point, the description of polarization has been concerned only with perfectly monochromatic waves. As mentioned previously, perfectly monochromatic beams are totally polarized with the time variation of the Cartesian components of the electric vector represented by an exact sine wave of infinite
length. In the case of a quasi-monochromatic wave, the spectrum consists of a narrow band of frequencies and the time variation of the electric field vector components is no longer represented by an infinite sine wave. The electric vector components of a quasi-monochromatic wave are expressed as [33]

\[ E_i = \tilde{E}_i(t) \cos [\omega_0 t + \delta_i(t)], \quad (2.14) \]

where \( \omega_0 \) is the central frequency and the amplitude, \( \tilde{E}_i(t) \), and phase, \( \delta_i(t) \), are functions of time. Over an interval of time, short enough to make the variation of \( \tilde{E}_i(t) \) and \( \delta_i(t) \) negligible and long enough to accommodate a large number of optical frequency cycles, a quasi-monochromatic wave behaves like a monochromatic wave and is therefore described by a Jones vector given as

\[ \vec{E}(t) = \begin{bmatrix} \tilde{E}_x(t)e^{i\delta_x(t)} \\ \tilde{E}_y(t)e^{i\delta_y(t)} \end{bmatrix}. \quad (2.15) \]

Equation (2.15) represents the Jones vector of a totally polarized quasi-monochromatic wave. Because of the time dependence, the Stokes parameters become averages over time intervals that are long compared to the optical frequency and are written as

\[ s_0 = \langle E_x^2 \rangle + \langle E_y^2 \rangle, \]
\[ s_1 = \langle E_x^2 \rangle - \langle E_y^2 \rangle, \]
\[ s_2 = \langle 2E_xE_y \cos(\delta_y - \delta_x) \rangle \quad (2.16) \]

and

\[ s_3 = \langle 2E_xE_y \sin(\delta_y - \delta_x) \rangle, \]
where the brackets ⟨⟩ signify the macroscopic time average. Due to the averaging procedure, the Stokes parameters no longer satisfy the equality of equation (2.13), but satisfy the inequality

\[ s_0^2 \geq s_1^2 + s_2^2 + s_3^2. \]  

(2.17)

Light can be monochromatic to a high degree (small spectral bandwidth) and still be unpolarized. An unpolarized beam of intensity \( I_0 \) has a Stokes vector \( \vec{S} = \{I_0, 0, 0, 0\} \). No Jones vector representation exists for unpolarized or partially polarized light [41]. A quantity that is important in characterizing partially polarized beams is referred to as the *degree of polarization*, and is defined as the ratio of the intensity of the totally polarized component to the total intensity of the wave. In terms of the Stokes parameters, the degree of polarization is given as

\[ P = \frac{s_1^2 + s_2^2 + s_3^2}{s_0^{1/2}}, \]  

(2.18)

where \( P \) varies from zero for unpolarized beams to one for totally polarized beams.

A third method for describing the polarization of light beams is known as the *coherency matrix* formulation. The two-by-two coherency matrix, \([J]\), is defined in terms of the time-dependent Cartesian Jones vector, \( \vec{E}(t) \) (equation (2.15)), as [33]

\[ [J] = \langle \vec{E}(t) \otimes \vec{E}^\dagger(t) \rangle \]
\[
\begin{bmatrix}
(\bar{E}_x \bar{E}_x^*) & (\bar{E}_x \bar{E}_y^*) \\
(\bar{E}_y \bar{E}_x^*) & (\bar{E}_y \bar{E}_y^*)
\end{bmatrix}
= \begin{bmatrix}
J_{xx} & J_{xy} \\
J_{yx} & J_{yy}
\end{bmatrix},
\]

(2.19)

where \( \otimes \) denotes the direct tensor product [45] of two matrices and \( \dagger \) denotes the adjoint [45] of a matrix, which is defined as the complex conjugate of the transpose of that matrix. Referring to equation (2.4) and (2.19), it is seen that the intensity of the beam is given as the sum of the squared amplitudes, or equivalently, as the trace of the coherency matrix. It is noted that the trace of a matrix is defined as the sum of the diagonal elements. The off diagonal elements describe the correlation (coherency) between the \( x \) and \( y \) components of the electric field vector. A totally unpolarized beam corresponds to zero correlation \( (J_{xy} = J_{yx} = 0) \) and a totally polarized beam corresponds to maximum correlation between the \( x \) and \( y \) components of the electric field [33].

Of the three methods used to describe the polarization of light, only the Jones vector is unable to describe partially polarized light. On the other hand, both the Stokes vector and the coherency matrix can describe partially polarized light. The Stokes parameters can be related to the coherency matrix parameters as [33]

\[
\begin{align*}
s_0 &= J_{xx} + J_{yy}, \\
s_1 &= J_{xx} - J_{yy}, \\
s_2 &= J_{xy} + J_{yx}.
\end{align*}
\]

(2.20)
and
\[ s_3 = -i (J_{zy} - J_{yz}) , \]
or in matrix form as
\[ \vec{S} = [A] \vec{J} , \]
where \([A]\) is given as
\[ [A] = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & -1 \\ 0 & 1 & 1 & 0 \\ 0 & -i & i & 0 \end{bmatrix} \] (2.22)
and \(\vec{J}\) is a four-by-one coherency vector whose elements are given as
\(\vec{J} = \{J_{xx}, J_{xy}, J_{yx}, J_{yy}\}\).

2.2 Optical Calculi

In the preceding section, three mathematical methods of describing the polarization of a quasi-monochromatic beam were introduced. The three methods introduced are the Jones vector, the Stokes vector, and the coherency matrix. The significance of utilizing vectors or matrices to describe polarization will be seen in this section.

Mathematically describing the interaction of polarized light with the optical elements of a system can be a difficult task. The Jones calculus, Mueller calculus, and the coherency matrix formulation are three mathematical techniques which aid in this task. When a light beam interacts with an optical system, the intensity and polarization are, in general, altered. The intensity and polarization of the beam can be represented by one of the three techniques discussed in the previous
section, the Jones and Stokes vectors and the coherency matrix. For the moment, the discussion will be restricted to the Jones matrix formulation.

Consider the case of a quasi-monochromatic light beam interacting with a non-depolarizing optical system. A depolarizing optical system is one in which the degree of polarization of the incident beam (before interaction with the optical system) is greater than the degree of polarization of the output beam (after interaction with the optical system) for at least one incident state of polarization. The properties of the incident beam will be described by a Jones vector, $\vec{E}_i$, in a Cartesian coordinate system $(x,y,z)$, where the $z$ axis is parallel to the incident beam. After the beam interacts with the optical system, the polarization and intensity of the outgoing beam will be altered. The outgoing beam properties are also described by a Jones vector, $\vec{E}_o$, in a Cartesian coordinate system $(x',y',z')$, where the $z'$ axis is parallel to the outgoing beam. In the absence of non-linear effects, the outgoing Jones vector, $\vec{E}_o$, is related to the incident Jones vector, $\vec{E}_i$, by the linear equations [33]

$$\vec{E}_{o,x'} = t_{11} \vec{E}_{i,x} + t_{12} \vec{E}_{i,y} \quad (2.23)$$

and

$$\vec{E}_{o,y'} = t_{21} \vec{E}_{i,x} + t_{22} \vec{E}_{i,y} \quad . \quad (2.24)$$

These equations can be written more concisely as

$$\vec{E}_o = [T] \vec{E}_i \quad , \quad (2.25)$$
where \([T]\) is a two-by-two transformation matrix called the Jones matrix of the optical system. The Jones matrix elements are, in general, complex.

A very similar case can be considered where the incident and outgoing beams are described by Stokes vectors \((\vec{S}_i, \vec{S}_o)\) instead of Jones vectors. An expression analogous to equation (2.25) is then used to describe the interaction of the beam with an optical system. The equation is

\[
\vec{S}_o = [M] \vec{S}_i ,
\]

where \(\vec{S}_o\) and \(\vec{S}_i\) represent the four-by-one Stokes vectors of the incident and outgoing beams and \([M]\) is the four-by-four transformation matrix known as the Mueller matrix. The sixteen elements of \([M]\) are real. If the optical system is non-depolarizing, the Mueller matrix description of the optical system is equivalent to the Jones matrix description and the Mueller matrix is given in terms of the Jones Matrix as

\[
[M] = [A] ([T] \otimes [T^*]) [A^{-1}] ,
\]

where \(\otimes\) represents the direct product of two matrices, the asterisk * represents the complex conjugate of a matrix, and the matrix \([A]\) is given by equation (2.22). In this case, only seven of the sixteen elements of the Mueller matrix are independent. If the optical system is a depolarizing system, all sixteen elements of the Mueller matrix may be independent.

As noted previously, the Jones formulation is not suitable for the description of partially polarized light or propagation through a depolarizing optical system.
On the other hand, the Mueller matrix formulation is completely general, and may be used to describe the propagation of partially polarized light through a depolarizing optical system. Naturally, the Mueller matrix formulation can also be used to handle the limiting case of completely polarized light through a non-depolarizing system. In this case, the Jones and Mueller formulation yield exactly the same results.

Another approach which is of interest is called the coherency matrix formulation \[33\], where the beam properties are described by the two-by-two coherency matrix and the Jones matrix is utilized to describe the interaction of the beam with an optical system. The coherency matrix formulation is capable of describing the propagation of partially polarized light through a non-depolarizing optical system. The basic equation utilized with the coherency matrix formulation to describe the propagation of light through an optical system is given as \[33\]

\[ [J_o] = [T][J_i][T^\dagger] \]

(2.28)

where \([J_i]\) and \([J_o]\) are the coherency matrices describing the intensity and polarization of the incident and outgoing beams and \([T]\) is the Jones matrix of the optical system. Tables 2.2 and 2.3 show the differences in the three approaches.

As seen in Tables 2.2 and 2.3, the Mueller calculus is more generally applicable than the other two methods. Because it can be utilized in depolarizing systems, the Mueller calculus has been applied to light scattering by small particles \[46–47\]. In the case of ellipsometry, both the Jones calculus and the Mueller
Table 2.2: Optical calculi – Description.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Description of Polarization</th>
<th>Description of Optical System</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jones coherency</td>
<td>$2 \times 1$ Jones vector, $\vec{E}_{x,y}$</td>
<td>$2 \times 2$ Jones matrix, $[T]$</td>
</tr>
<tr>
<td></td>
<td>$2 \times 2$ coherency matrix, $[J]$</td>
<td>$2 \times 2$ Jones matrix, $[T]$</td>
</tr>
<tr>
<td>Mueller</td>
<td>$4 \times 1$ Stokes vector, $\vec{S}$</td>
<td>$4 \times 4$ Mueller matrix, $[M]$</td>
</tr>
</tbody>
</table>

Table 2.3: Optical calculi – Range of validity.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Range of Validity</th>
<th>Basic Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jones coherency</td>
<td>totally polarized light, non-depolarizing optical system</td>
<td>$\vec{E}<em>{x,y} = [T] \vec{E}</em>{x,z,y}$</td>
</tr>
<tr>
<td>Mueller</td>
<td>partially polarized light, depolarizing optical system</td>
<td>$\vec{S} = [M] \vec{S}_o$</td>
</tr>
<tr>
<td>Mueller</td>
<td></td>
<td>$[J] = [T][J]\dagger$</td>
</tr>
</tbody>
</table>

Calculi have been utilized. If the effects of imperfect optical components on ellipsometry measurements are to be considered, the Jones calculus is inadequate, and the Mueller calculus must be used. Since in practical optical systems the optical components are not perfect, the Mueller calculus will be utilized throughout the remainder of this study.
2.3 **Mueller Calculus**

As mentioned in the previous section, Mueller calculus is a mathematical technique that is utilized to describe the change in intensity and polarization of a light beam as it passes through or is redirected by the elements of an optical system. The fundamental equation used in Mueller calculus is given as

\[
\vec{S}_o = [M] \vec{S}_i ,
\]  

(2.29)

where \( \vec{S}_i \) is the four parameter Stokes vector of the incident beam, \( \vec{S}_o \) is the Stokes vector of the beam emerging from the optical system, and \([M]\) is the four-by-four Mueller matrix of the optical system. Therefore, by simply knowing the Mueller matrix of an optical component, one can calculate the effects of that optical system on beam intensity and polarization. If a beam passes through a series of optical components, the effects on polarization and intensity can be calculated by successive applications of equation (2.29). Equivalently, the series of optical components can be treated as a single optical system and can be described by a single Mueller matrix. The Mueller matrix of such a series of \( N \) components is given as [33,41]

\[
[M] = [M_N][M_{N-1}][M_{N-2}] \ldots [M_1] ,
\]  

(2.30)

where \([M]\) is the Mueller matrix of the entire optical system and \([M_i]\) represents the Mueller matrices of the individual optical components. The order of multiplication is important and must be in reverse order that the beam encounters the
optical device. Thus, in equation (2.30), device 1 is encountered first and device N is encountered last.

As stated in Section 2.1, the intensity of a beam is given by the first parameter of its Stokes vector. It can be seen from equation (2.29) that if an unpolarized beam ($\vec{S}_i = \{I_0, 0, 0, 0\}$) is incident upon an optical system, $[M]_{1,1}$ represents the ratio of the intensities of the outgoing and incident beams.

The Stokes vectors of equation (2.29) ($\vec{S}_i, \vec{S}_o$) represent the beam properties of the incident and outgoing beams in their respective coordinate systems. Therefore, the Mueller matrix of an element is defined by its orientation to the incident $(x,y,z)$ and outgoing $(x',y',z')$ coordinate systems. The coordinate systems are defined such that the $z$ and $z'$ axes are parallel to the incident and outgoing beams, respectively. If the optical system does not alter the beam direction, leaving $z$ and $z'$ parallel, the $(x,y,z)$ and $(x',y',z')$ coordinate systems are also parallel. Otherwise, the $x$ and $x'$ axes are chosen to coincide with the plane formed by the $z$ and $z'$ axes. A Stokes vector in the $(x,y,z)$ coordinate system can be transformed to the $(x',y',z)$ coordinate system by the equation [33,41]

$$\vec{S}_{x',y'} = [R(\alpha)] \vec{S}_{x,y},$$  \hspace{1cm} (2.31)

where $[R(\alpha)]$ is called the rotation matrix and is given as

$$[R(\alpha)] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\alpha) & \sin(2\alpha) & 0 \\ 0 & -\sin(2\alpha) & \cos(2\alpha) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.$$  \hspace{1cm} (2.32)

The term $\alpha$ is the angle between the $x$ and $x'$ axes when the $(x',y',z')$ coordinate
system is rotated positively about the z (or z') axis according to the right hand rule. If the Mueller matrix of an optical element, such as a polarizer, is known with respect to one azimuthal orientation, its Mueller matrix for any azimuthal orientation can be found by applying equation (2.31) twice. Azimuthal orientation refers to a device's angular position as it is rotated about the z axis (beam direction). The Mueller matrix of a device in a general orientation, \([M]\), is given as

\[
[M] = [R(-\alpha)][M_0][R(\alpha)],
\]  

(2.33)

where \([M_0]\) is the Mueller matrix of the device in its principle orientation and \(\alpha\) is the azimuthal angle of the device with respect to the coordinate system. For example, the Mueller matrix of an ideal polarizer aligned with its transmission axis parallel to the z axis is given as

\[
[P_0] = \frac{1}{2} \begin{bmatrix} 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix}.
\]  

(2.34)

The Mueller matrix of a polarizer aligned with its transmission axis aligned at an angle \(\alpha\) with respect to the z axis is found by applying equation (2.33) and is given as

\[
[P] = [R(-\alpha)][P_0][R(\alpha)]
= \frac{1}{2} \begin{bmatrix} 1 & c & s & 0 \\ c & c^2 & cs & 0 \\ s & sc & s^2 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},
\]  

(2.35)

where \(c = \cos(2\alpha)\) and \(s = \sin(2\alpha)\).
The Mueller matrices of devices are based upon a phenomenological approach and are found from experimental results. The Mueller matrix of an element can be found by considering its interaction with four independent types of polarization [41]. The Mueller matrices of some common optical components are shown in Appendix A.

2.4 Reflection of Light From a Surface

As stated in the previous section, Mueller calculus can be utilized to describe the interaction of polarized light with optical components. Because this study is primarily concerned with the determination of the optical properties of a material through the analysis of polarized light reflected from a sample, it is of interest to describe the process of reflection in more detail. The equations presented in this section will be valid only for perfectly smooth surfaces.

When a light beam is incident upon a surface at a given angle of incidence (θ), part of that beam is reflected and part is transmitted, as shown in Figure 2.1. The incident, reflected and transmitted beams are all located in the plane of incidence, where the plane of incidence is defined as the plane formed by the incident light vector and the vector normal to the sample surface. The angle that the reflected beam forms with the outward surface normal is called the angle of reflection and the angle that the transmitted (refracted) beam makes with the inward surface normal is called the angle of refraction. The angle of reflection is equal in magnitude to the angle of incidence. The angle of refraction is denoted
by the symbol $\theta'$ and is related to the angle of incidence ($\theta$) by Snell's Law as

$$\tilde{m} \sin(\theta) = \tilde{m}' \sin(\theta') ,$$

(2.36)

where $\tilde{m} = n - ik$ is the complex refractive index of the ambient medium and $\tilde{m}'$ is the complex refractive index of the surface. The imaginary part of the refractive index, $k$, is sometimes called the absorptive index. In this study, the ambient medium is air or some inert gas which are all assumed to have a refractive index $\tilde{m} = 1.0 - 0i$. Note that the angle of refraction ($\theta'$) is, in general, complex because $\tilde{m}'$ is complex.

As stated earlier in this chapter, the intensity and polarization of a light beam are described by the electric field vector components in two orthogonal directions which are perpendicular to the direction of propagation. Therefore, reflection from the surface can be described by the two electric field vector
components of the reflected beam. The coordinate system is chosen such that one component is perpendicular to the plane of incidence and one component is parallel to the plane of incidence, as shown in Figure 2.2. The electric field components, described as ratios of the reflected beam to the incident beam, are given by Fresnel's Laws of Reflection as [48]

\[
\tilde{r}_s = \left[ \frac{\tilde{E}'}{\tilde{E}_s} \right] = -\frac{\sin(\theta - \theta')}{\sin(\theta + \theta')} \tag{2.37}
\]

and

\[
\tilde{r}_p = \left[ \frac{\tilde{E}'}{\tilde{E}_p} \right] = \frac{\tan(\theta - \theta')}{\tan(\theta + \theta')} \tag{2.38}
\]

The subscripts \( s \) and \( p \) represent polarization perpendicular and parallel to the plane of incidence, respectively and \( \tilde{E} \) and \( \tilde{E}' \) are the electric field components of the incident and reflected beam, respectively. Note that \( \tilde{r}_s \) and \( \tilde{r}_p \) are, in general,
complex quantities which describe the amplitude and phase change of the electric
field vector upon reflection. Because the intensity of a beam is proportional to
the square of the electric field vector amplitude, the intensity reflectances are
given as
\[ R_\parallel = |\vec{r}_p|^2 \] (2.39)
and
\[ R_\perp = |\vec{r}_s|^2 . \] (2.40)
The subscripts $\parallel$ and $\perp$ represent polarization parallel and perpendicular to the
plane of incidence. The reflectances, $R_\parallel$ and $R_\perp$, represent the fraction of the
intensity of a beam which is reflected from a surface. The reflectances are given
in terms of real numbers as [49]
\[ R_\parallel = \frac{a^2 + b^2 - 2a \sin(\theta) \tan(\theta) + \sin^2(\theta) \tan^2(\theta)}{a^2 + b^2 + 2a \sin(\theta) \tan(\theta) + \sin^2(\theta) \tan^2(\theta)} R_\perp \] (2.41)
and
\[ R_\perp = \frac{a^2 + b^2 - 2a \cos(\theta) + \cos^2(\theta)}{a^2 + b^2 + 2a \cos(\theta) + \cos^2(\theta)} , \] (2.42)
where
\[ a - ib = \left[(n - ik)^2 - \sin^2(\theta)\right]^{1/2} . \] (2.43)
Equation (2.43) can be used to solve for $a$ and $b$ as
\[ 2a^2 = \left[(n^2 - k^2 - \sin^2(\theta))^2 + 4n^2k^2\right]^{1/2} + [n^2 - k^2 - \sin^2(\theta)] \] (2.44)
and
\[ 2b^2 = \left[(n^2 - k^2 - \sin^2(\theta))^2 + 4n^2k^2\right]^{1/2} - [n^2 - k^2 - \sin^2(\theta)] . \] (2.45)
It can be shown from equations (2.41)-(2.45) that a unique relation exists between the two reflectance components at an angle of incidence of 45 degrees. The relation, called the *specularity index*, is given as

\[
\left[ \frac{R^2_\perp}{R^2_\parallel} \right]_{\theta=45^\circ} = 1.0
\]

(2.46)

and holds for all smooth, flat surfaces, regardless of the refractive index of the material. The relation given by equation (2.46) does not hold for surfaces which are not perfectly smooth. In fact, Chapter 4 will discuss methods of characterizing surface roughness based upon deviation of the measured specularity index from unity. The complex ellipsometric parameter of a surface \((\rho e^{i\Delta})\) is defined as the ratio of the electric field reflectivities in the plane parallel \((p)\) and perpendicular \((s)\) to the plane of incidence, namely:

\[
\frac{\tilde{r}_p}{\tilde{r}_s} = \frac{|\tilde{r}_p|e^{i\epsilon_p}}{|\tilde{r}_s|e^{i\epsilon_s}} = \rho e^{i\Delta} ,
\]

(2.47)

where \(\tilde{r}_p\) and \(\tilde{r}_s\) were defined previously. Therefore, \(\rho\) and \(\Delta\) determine the differential changes in amplitude and phase, respectively, experienced upon reflection by the components (parallel and perpendicular) of the electric vector.

The ellipsometric parameters are related to the refractive index as [49–50]

\[
\rho^2 = \frac{R_\parallel}{R_\perp}
\]

\[
= \frac{a^2 + b^2 - 2a \sin(\theta) \tan(\theta) + \sin^2(\theta) \tan^2(\theta)}{a^2 + b^2 + 2a \sin(\theta) \tan(\theta) + \sin^2(\theta) \tan^2(\theta)}
\]

(2.48)

and

\[
\tan(\Delta) = \frac{-2b \sin(\theta) \tan(\theta)}{a^2 + b^2 - \sin^2(\theta) \tan^2(\theta)} ,
\]

(2.49)
where \( a \) and \( b \) are given by equations (2.44)-(2.45). The real \((n)\) and imaginary \((k)\) parts of the complex refractive index are expressed in terms of \( \rho \) and \( \Delta \) by the relation [50]

\[
2n^2 = \left[ (a^2 - \delta^2 + \sin^2(\theta))^2 + 4a^2\delta^2 \right]^{1/2} + a^2 - \delta^2 + \sin^2(\theta) \tag{2.50}
\]

and

\[
k = \frac{ab}{n}, \tag{2.51}
\]

where

\[
a = \frac{(1 - \rho^2) \sin(\theta) \tan(\theta)}{1 + 2\rho \cos(\Delta) + \rho^2} \tag{2.52}
\]

and

\[
b = \frac{2\rho \sin(\theta) \tan(\theta) \sin(\Delta)}{1 + 2\rho \cos(\Delta) + \rho^2}. \tag{2.53}
\]

Therefore, once \( \rho \) and \( \Delta \) are determined for a bare substrate from ellipsometry measurements, the complex refractive index of the substrate can be computed from equations (2.50)-(2.53).

The terms introduced in this section can be used to fully describe the reflection of light from a smooth sample surface. The Mueller matrix representing the reflection of light from a surface, \([S]\), is given as [33]

\[
[S] = \frac{1}{2} \begin{bmatrix}
R_{\parallel} + R_{\perp} & R_{\parallel} - R_{\perp} & 0 & 0 \\
R_{\parallel} - R_{\perp} & R_{\parallel} + R_{\perp} & 0 & 0 \\
0 & 0 & 2\sqrt{R_{\parallel}R_{\perp}} \cos(\Delta) & 2\sqrt{R_{\parallel}R_{\perp}} \sin(\Delta) \\
0 & 0 & -2\sqrt{R_{\parallel}R_{\perp}} \sin(\Delta) & 2\sqrt{R_{\parallel}R_{\perp}} \cos(\Delta)
\end{bmatrix}
= \frac{R_{\perp}}{2} \begin{bmatrix}
\rho^2 + 1 & \rho^2 - 1 & 0 & 0 \\
\rho^2 - 1 & \rho^2 + 1 & 0 & 0 \\
0 & 0 & 2\rho \cos(\Delta) & 2\rho \sin(\Delta) \\
0 & 0 & -2\rho \sin(\Delta) & 2\rho \cos(\Delta)
\end{bmatrix}. \tag{2.54}
\]
It is seen that the Mueller matrix of a surface, \([S]\), is dependent upon the refractive index of the sample, as well as the angle of incidence. When determining the refractive index of a material by reflection measurements, the parameters which are measured can include \(R_{\parallel}, R_{\perp}, \rho,\) and \(\Delta\). Therefore, it is of interest to study these parameters in more detail. In Figure 2.3, the reflectivities, \(R_{\parallel}\) and \(R_{\perp}\), are plotted versus angle of incidence \((\theta)\). The two lower curves correspond to the reflectivities of a dielectric material (non-conductor), which is characterized by a zero value for the absorptive index, \(k\). The two upper curves correspond to the reflectivities of a conductor, such as aluminum. It is seen that conductors are characterized by high reflectivities. As can be inferred from this figure, the reflectivities in both planes of polarization are equal at normal incidence \((\theta = 0^\circ)\) and both increase to a value of one at grazing incidence \((\theta = 90^\circ)\) for all materials. The parallel component of reflectivity \((R_{\parallel})\) exhibits a minimum at some angle of incidence, with this minimum being exactly zero for dielectric materials. The angle of incidence at which the minimum occurs is called the Brewster angle. The ellipsometric parameters of a surface, \(\rho\) and \(\Delta\), are plotted versus angle of incidence in Figures 2.4–2.5 for several different refractive indices. The first ellipsometric parameter, \(\rho\), is seen to have the value of 1.0 for both normal and grazing incidence. The value of \(\rho\) also has a minimum at some angle of incidence. For dielectric materials, this minimum is exactly zero and it occurs at the Brewster angle. For conducting materials, this minimum will not
Figure 2.3: Reflectivities versus angle of incidence for two different refractive indices. The two lower curves correspond to the reflectivities from a dielectric with refractive index \( \tilde{m} = 1.8 - 0i \) and the two upper curves correspond to reflectivities from a metal with refractive index \( \tilde{m} = 2 - 8i \).
Figure 2.4: First ellipsometric parameter ($\rho$) versus angle of incidence for three different refractive indices: $m = 2 - 0i$, $\tilde{m} = 2 - 1i$, and $\tilde{m} = 2 - 5i$. 
Figure 2.5: Second ellipsometric parameter ($\Delta$) versus angle of incidence for three different refractive indices: $\tilde{m} = 2 - 0i$, $\tilde{m} = 2 - 1i$, and $\tilde{m} = 2 - 5i$. 
be located exactly at the Brewster angle. In Figure 2.5, the phase change on reflection ($\Delta$) is plotted versus angle of incidence. It is seen that $\Delta$ has a value of $180^\circ$ at normal incidence and $0^\circ$ at grazing incidence. For dielectric materials ($k = 0$), the value of $\Delta$ changes discontinuously from a value of $180^\circ$ to $0^\circ$ at the Brewster angle. As the value of the absorptive index ($k$) increases (material becomes more conducting), the change in $\Delta$ becomes more gradual. The angle of incidence at which the phase change ($\Delta$) is equal to $90^\circ$ or $\pi/2$ is called the principal angle. The Brewster angle and principal angle are only equal to each other for dielectric materials. The Brewster angle ($\beta$) is found as the angle of incidence which minimizes the parallel component of reflectivity, and is given as the physically significant root of a cubic equation, namely [51]

\[2(p^2 + q)v^3 + p^2(p^2 - 3)v^2 - 2p^4v + p^4 = 0 \quad (2.55)\]

where $v = \sin^2(\beta)$. The principal angle ($\gamma$) is found as the angle of incidence where $\Delta = \pi/2$ and is also given as the physically significant root of a cubic equation, namely [51]

\[2(q + 1)w^3 - (p^2 + 4q + 1)w^2 + 2(p^2 + q)w - p^2 = 0 \quad (2.56)\]

where $w = \sin^2(\gamma)$. The terms $p$ and $q$ are given in terms of the refractive index as

\[p = n^2 + k^2 \quad (2.57)\]

and

\[q = n^2 - k^2 . \quad (2.58)\]
The Brewster angle and the principal angle are very close to the same angle for most materials. In fact, for a refractive index of \( n = 3.0 - 0.4i \), Humphreys-Owen [51] states that the difference is less than 0.1°.

A semi-transparent material is characterized by \( \cos(\Delta) \) approaching \( \pm 1 \) for all angles of incidence, or equivalently, by the imaginary part \( (k) \) of the refractive index approaching zero. If the material is completely transparent, the material is called a dielectric, and the imaginary part \( (k) \) of the refractive index is identically zero. The real part \( (n) \) of the refractive index of a dielectric is found by letting \( \cos(\Delta) = -1 \) for angles of incidence less than the Brewster angle and \( \cos(\Delta) = +1 \) for angles of incidence greater than the Brewster angle. For angles of incidence less than the Brewster angle, the real part \( (n) \) of the refractive index is given as

\[
\begin{align*}
n & = \sin(\theta) \left[ \left( \frac{1 + \rho}{1 - \rho} \right)^2 \tan^2(\theta) + 1 \right]^{1/2},
\end{align*}
\]  

and for angles of incidence greater than the Brewster angle, \( n \) is given as

\[
\begin{align*}
n & = \sin(\theta) \left[ \left( \frac{1 - \rho}{1 + \rho} \right)^2 \tan^2(\theta) + 1 \right]^{1/2}.
\end{align*}
\]  

In fact, it may be shown that the complex refractive index \( (n - ik) \) of any general material (not only a dielectric material) is given in terms of the complex ellipsometric parameter \( (\rho e^{i\Delta}) \) by [33]

\[
\begin{align*}
n - ik & = \sin(\theta) \left[ \left( \frac{1 - \rho e^{i\Delta}}{1 + \rho e^{i\Delta}} \right)^2 \tan^2(\theta) + 1 \right]^{1/2}.
\end{align*}
\]
Chapter 3
Development of Equations

The optical technique utilized for this study is known as ellipsometry. Ellipsometry is generally concerned with the measurement of the state of polarization of a light beam. The state of polarization of a light beam is of interest because it conveys information about the system which interacted with the beam. Two of the most common types of ellipsometry are known as null ellipsometry and photometric ellipsometry. In null ellipsometry, information about the system under study is obtained by finding settings of the optical components (polarizer, compensator, analyzer) which extinguish (null) the intensity through the ellipsometer system. In photometric ellipsometry, system information is obtained by measuring the intensity of light through the ellipsometer system under different settings of the optical components (polarizer, analyzer). A compensator is a necessary part of a null ellipsometer but is not needed for a photometric ellipsometer. For the purposes of convenience, the definition of certain typical optical components is given here. A compensator is an optical device which introduces a phase shift.
between the \( x \) and \( y \) component of the electric field. A quarter wave plate is a special type of compensator which introduces a phase shift of 90 degrees. A linear polarizer is a device which converts a beam of light into a linearly polarized beam regardless of the polarization form of the incident beam. The photometric ellipsometry technique is to be utilized for this study. A discrete Fourier transform will be used to analyze the data and all equations will be derived in terms of the Fourier coefficients.

The basic mathematical techniques for the description of the propagation of light through an optical system have been presented in Chapter 2. In particular, the Mueller calculus formulation has been described in detail. In this chapter, the Mueller calculus will be utilized to describe the propagation of light through the PSA ellipsometer system designed for this study. The equations developed in this chapter will be used to evaluate the refractive index of the sample from experimental measurements.

### 3.1 Mueller Calculus of a PSA Ellipsometer

The Mueller calculus formulation can be utilized to describe the propagation of light through the PSA ellipsometer system designed for this study. The acronym PSA refers to the polarizer-sample-analyzer that constitute the main optical elements of an ideal ellipsometer system. A schematic of the ellipsometer utilized for this study is shown in Figure 3.1. Although an ideal PSA ellipsometer consists of only a polarizer, sample, and analyzer, many more optical components may
be involved in an actual PSA ellipsometer. In addition to the polarizer, sample, and analyzer, the system in Figure 3.1 consists of collection optics (mirrors), windows, and a monochromator. These additional components may alter the polarization of the beam, thereby affecting the experimental results.

As stated in Chapter 2, the effects of a series of optical components, such as in the ellipsometer system of Figure 3.1, may be described by a single Mueller matrix (see equation (2.30)). Therefore, the Mueller matrix of an ideal PSA ellipsometer is given as

$$[M_{PSA}] = [A][S][P] ,$$  \hspace{1cm} (3.1)

where $[M_{PSA}]$ represents the combination Mueller matrix of the entire ellipsometer system, $[A]$ represents the Mueller matrix of the analyzer (analyzing polarizer), $[S]$ reflection from the sample of interest, and $[P]$ the polarizer. When considering a non-ideal ellipsometer system, the effects of the collection optics, windows, and monochromator must be taken into account. Therefore, the Mueller matrix of the non-ideal ellipsometer system shown in Figure 3.1 is given as

$$[M] = [D][A][W_2][S][W_1][P][L] ,$$  \hspace{1cm} (3.2)

where $[M]$ represents the Mueller matrix of the entire ellipsometer system, $[D]$ the detector optics ($P_2, C_2$, and monochromator), $[A]$ the analyzer (analyzing polarizer), $[S]$ the sample of interest, $[P]$ the polarizer, and $[L]$ represents the light source optics (including light source, $P_1$, and $C_1$). The matrices $[W_1]$ and $[W_2]$ represent the Mueller matrices of the entrance and exit windows of the high
Figure 3.1: Schematic of PSA ellipsometer centered around a high temperature furnace. LS is the Xenon arc light source, C1 and C2 are curved first surface mirrors (200 mm focal length), P1 and P2 are plane first surface mirrors, W1 and W2 are quartz cell windows of the furnace, P and A are the polarizer and analyzer, M is the monochromator, D is the detector, S is the sample, I is the iris diaphragm, F is the cut-on filter, and LC is the light chopper.
temperature unit. The \([D]\) and \([L]\) matrices depend upon the coatings of the mirrors, the angle of reflection from these mirrors, and \([D]\) also depends strongly on the specific design of the monochromator. For convenience the Mueller matrices of the optical components are shown in Appendix A.

Note that equation (3.2) reduces to equation (3.1) if \([D]\), \([L]\), \([W_2]\), and \([W_1]\) are equal to the identity matrix. Therefore, the deviation of these matrices from the identity matrix represents the deviation of the actual ellipsometer system from the ideal system.

As noted previously, the technique to be used for this study is photometric ellipsometry, where the intensity through the ellipsometer system yields information about the system. As discussed in Chapter 2, the (1,1) element of a Mueller matrix represents the ratio of the intensity of the transmitted beam to the intensity of the incident beam if the incident beam is completely unpolarized. Since the light source utilized for this study is largely unpolarized, the (1,1) element contains the information necessary to characterize the system.

3.2 Discrete Fourier Transform

It can be shown from equations (3.1) and (3.2) that as the polarizer is rotated, the intensity through an ideal PSA ellipsometer varies sinusoidally [52] with a period of 180 degrees. The intensity variation through a non-ideal PSA ellipsometer is very similar to that of an ideal system, except that a higher frequency component appears, having a period of 90 degrees. Therefore, the intensity through a general
PSA ellipsometer can be written as a truncated Fourier series, namely

\[ I(P) = a_0 [1 + a_2 \cos(2P) + b_2 \sin(2P) + a_4 \cos(4P) + b_4 \sin(4P)] , \tag{3.3} \]

where the normalized Fourier coefficients \((a_2, b_2, a_4, \text{ and } b_4)\) can be related to the optical properties of the sample.

The Fourier coefficients may be calculated from a set of experimental data by a simple discrete Fourier transform as

\[ a_0 = \frac{1}{N} \sum_{k=1}^{N} I_k , \tag{3.4} \]

\[ \tilde{a}_n = \frac{2}{N} \sum_{k=1}^{N} I_k \cos(nP_k) \tag{3.5} \]

and

\[ \tilde{b}_n = \frac{2}{N} \sum_{k=1}^{N} I_k \sin(nP_k) , \tag{3.6} \]

where \(I_k\) is the experimental intensity readings at equally spaced azimuthal settings of the polarizer, \(P_k\), and \(N\) is the number of experimental measurements. The normalized Fourier coefficients \((a_n, b_n)\) are related to the standard (non-normalized) Fourier coefficients \((\tilde{a}_2, \tilde{b}_2)\) as

\[ a_n = \frac{\tilde{a}_n}{a_0} \tag{3.7} \]

and

\[ b_n = \frac{\tilde{b}_n}{a_0} . \tag{3.8} \]

The Fourier analysis given by equations (3.4)–(3.8) is equivalent to a least squares fitting procedure for evenly spaced data [53].
Because the Fourier coefficients \((a_2, b_2, a_4, b_4)\) fully describe the intensity through a PSA ellipsometer, all equations can be described in terms of the Fourier coefficients with no loss of generality.

### 3.3 Fourier Series of an Ideal PSA Ellipsometer System

An ideal PSA ellipsometer system consists of a polarizer-sample-analyzer only, where the source and detector optics ([L] and [D]) and windows ([W_1] and [W_2]) have no influence on the beam polarization. The polarizer and analyzer are also considered to be ideal (i.e. linear polarizers with zero leakage). These assumptions are equivalent to assuming that the matrices \([L], [D], [W_1],\) and \([W_2]\) in equation (3.2) are equal to the identity matrix. Therefore, the system Mueller matrix will be given as

\[
[M] = [A][S][P]. 
\] (3.9)

Under these circumstances, the intensity of the beam reaching the detector (equal to the \((1,1)\) element of matrix \([M]\) in equation (3.9)) is given as

\[
I_{PSA}(P, A) = C_1 k_A k_P R_{\perp} \left[ \rho^2 \cos^2(P) \cos^2(A) + \sin^2(P) \sin^2(A) 
+ \frac{\rho}{2} \cos(\Delta) \sin(2P) \sin(2A) \right], 
\] (3.10)

where \(k_A\) and \(k_P\) are the first principal transmittances of the analyzer and polarizer, \(R_{\perp}\) is the perpendicular component of the reflectivity, \(\rho\) and \(\Delta\) the ellipsometric parameters of the sample, \(P\) and \(A\) the polarizer and analyzer azimuths.
angles, and \( C_1 \) is a constant. It is noted that the parameters \( \rho \) and \( \Delta \) are defined as the ratio of the reflectivities in the plane parallel (\( p \)) and perpendicular (\( s \)) to the plane of incidence, namely:

\[
\frac{\tilde{r}_p}{\tilde{r}_s} = \frac{|\tilde{r}_p|e^{i\phi_p}}{|\tilde{r}_s|e^{i\phi_s}} = \rho e^{i\Delta},
\]

where

\[
\tilde{r}_{p,s} = \begin{bmatrix} \tilde{E}_r \\ \tilde{E}_i \end{bmatrix}_{p,s},
\]

with \( \tilde{E}_r, \tilde{E}_i \) being the reflected and incident electric field vectors in the plane parallel and perpendicular to the plane of incidence. It is also noted that the polarizer azimuths, \( P \) and \( A \), are the azimuthal angles between the transmission axis of the polarizer and the plane of incidence. The direction of positive azimuth is counterclockwise when looking into the oncoming beam.

Equation (3.10) can also be written in terms of a truncated Fourier series (equation (3.3)), with the Fourier coefficients given as

\[
a_2 = \frac{\rho^2 - \tan^2(A)}{\rho^2 + \tan^2(A)},
\]

\[
b_2 = \frac{2\rho \cos(\Delta) \tan(A)}{\rho^2 + \tan^2(A)},
\]

\[
a_4 = 0
\]

and

\[
b_4 = 0.
\]

Therefore, the ellipsometric parameters, \( \rho \) and \( \Delta \), can be found from the Fourier series.
coefficients as
\[ \rho = \tan(A) \sqrt{\frac{1 + a_2}{1 - a_2}} \]  \hspace{1cm} (3.17)
and
\[ \cos(\Delta) = \frac{b_2}{\sqrt{1 - a_2^2}} \]  \hspace{1cm} (3.18)

Now that the ellipsometric parameters are defined in terms of the Fourier coefficients, it is a simple two-step procedure to calculate the ellipsometric parameters from a set of experimental intensity data. Step 1 is to calculate the Fourier coefficients using equations (3.4)-(3.8) and Step 2 is to use these Fourier coefficients to calculate the ellipsometric parameters from equations (3.17) and (3.18). Note that in order to use this Fourier coefficient technique, the experimental intensity data must be taken at evenly spaced intervals of the polarizer setting (P) for a full revolution of the polarizer [53].

3.4 Source and Detector Optics

As mentioned in the previous section, the source and detector optics influence the beam polarization, with this influence being described by the [L] and [D] matrices. From equation (3.2), it can be seen that only the first row of the [D] matrix and the first column of the [L] matrix influence the measured intensity, where the measured intensity is given by the (1,1) element of the system Mueller matrix. Furthermore, if the analyzer and polarizer are considered ideal (i.e. zero
leakage), only the first three elements of this first row and first column influence the ellipsometer intensity.

The effects of either one of these matrices can be nullified by rotating the polarizing element not associated with it. In other words, the ellipsometer intensity (normalized) varies as the polarizer is rotated, with this intensity variation being independent of the matrix \([D]\). Similarly, if the analyzer is rotated, the intensity variation will be independent of the matrix \([L]\). Since a grating monochromator has a much larger influence on beam polarization than does reflection from a high quality mirror, it is preferable for the purposes of this study to fix the analyzer position and rotate the polarizer.

3.4.1 Calculation of the \([L]\) Matrix

Since the analyzer will be fixed and the polarizer rotated, only the \([L]\) matrix will influence the measured intensity. The elements of the \([L]\) matrix may be calculated by applying the basic rules of Mueller calculus. Referring to Figure 3.1, the \([L]\) matrix can be written as

\[
[L] = [R(-90^\circ)][R(\gamma)][C_1][R(\beta)][P_1][R(\alpha)] ,
\]

where \([R(\phi)]\) is the rotation matrix and the matrices \([C_1]\) and \([P_1]\) designate reflection from mirrors \(C_1\) and \(P_1\) at their respective angles of incidence (see Appendix A for the form of a reflection and rotation matrix). The angle \(\alpha\) is the angle that \(\hat{n}_1\) must be rotated around axis LS-P1 to lie in the vertical plane, where \(\hat{n}_1\) is the vector normal to the LS-P1-C1 plane. The angle \(\beta\) is the angle
that \( \hat{n}_1 \) must be rotated around axis \( P_1 - C_1 \) to become parallel to \( \hat{n}_2 \), where \( \hat{n}_2 \) is the vector normal to the \( P_1 - C_1 - P \) plane. The angle \( \gamma \) is the angle that \( \hat{n}_2 \) must be rotated around axis \( C_1 - P \) to lie in the vertical plane.

The angles \( \alpha, \beta, \text{ and } \gamma \) can be calculated by assigning cartesian coordinates to points \( P_1, C_1, \text{ and } S \) and then using the appropriate analytic geometry relations. The angles \( \alpha, \beta, \text{ and } \gamma \) were found to be 15.6°, 53.3°, and 13.8°, respectively. Similarly, the angles of reflection from mirrors \( P_1 \) and \( C_1 \) (\( \phi_1 \) and \( \phi_2 \)) were found to be 29.5° and 29.1°, respectively. The calculation of these angles is shown in Appendix B.

Using these angles and the appropriate matrices from equation (3.19), the elements of \([L]\) can be computed. Because the ellipsometer intensity is always normalized before analysis, the \([L]\) matrix can be normalized by the \((1,1)\) element, with no loss of generality. Therefore, the two quantities which describe the source optics will be called \( l_1 \) and \( l_2 \). These two quantities are described in terms of the elements of \([L]\) as

\[
l_1 = \frac{l_{21}}{l_{11}} \tag{3.20}
\]

and

\[
l_2 = \frac{l_{31}}{l_{11}}, \tag{3.21}
\]

where \( l_{ij} \) represents the \((i,j)\) element of matrix \([L]\). The source optics parameters, \( l_1 \) and \( l_2 \), depend not only upon the angles defined previously (\( \alpha, \beta, \gamma, \phi_1, \text{ and } \phi_2 \)), but also upon the nature of the reflecting surfaces of \( P_1 \) and \( C_1 \). In this instance,
P₁ and C₁ are first surface aluminum reflectors with a 200 nm thick magnesium fluoride (MgF₂) overcoat. The optical properties of aluminum [54] and MgF₂ [55] are shown in Figures 3.2 and 3.3 as a function of wavelength. The reflection matrices \([C₁]\) and \([P₁]\) are defined in terms of their ellipsometric parameters (\(\rho\) and \(\Delta\)) as shown in Appendix A. The ellipsometric parameters are calculated using the Fresnel equations describing reflectance of polarized light from a substrate with a transparent overcoat [33], assuming that the multiply reflected beams from the Al substrate and MgF₂ overcoat combine coherently. Coherent combination of the multiply reflected beams will only occur if the coherence length \(l_c\) of the light striking the detector is large compared to the thickness of the transparent MgF₂ overcoat of the mirrors. The coherence length is given as [48]

\[
l_c = \frac{\lambda^2}{\Delta \lambda},
\]

(3.22)

where \(\lambda\) and \(\Delta \lambda\) are the wavelength and spectral bandwidth, respectively of the light striking the detector. The spectral bandwidth (\(\Delta \lambda\)) of the light is determined by the properties of the grating monochromator and the width of the entrance and exit slits of the monochromator. The monochromator grating utilized in this study has a reciprocal dispersion of 6.4 nm/mm. Therefore, the spectral bandwidth of the beam striking the detector is approximately 3.2 nm for a slit width of 0.5 mm. This spectral bandwidth yields a coherence length of 50,000–150,000 nm when the wavelength is 400–700 nm. Because the coherence length of the beam is long compared to the thickness of the MgF₂ overcoat
Figure 3.2: Refractive index of aluminum from CRC Handbook [54].
Figure 3.3: Refractive index of magnesium fluoride [55]. Note that MgF$_2$ is transparent, and therefore, only the real part of the refractive index exists.
(200 nm), it can be assumed that coherent interference of the multiply reflected beams does occur. With all matrices in equation (3.19) defined, the source parameters, \( l_1 \) and \( l_2 \), can be calculated from a simple matrix multiplication. These source parameters are shown as a function of wavelength in Figure 3.4.

### 3.4.2 Effects of Source and Detector Optics

If the source and detector optics are not considered ideal, the system Mueller matrix is given as

\[
[M] = [D][A][S][P][L] ,
\]

where \([D]\) and \([L]\) are considered to be general matrices with elements \(d_{ij}\) and \(l_{ij}\), respectively. Under these conditions, the intensity of the beam reaching the detector (equal to the (1,1) element of matrix \([M]\) in equation (3.23)) is given as

\[
I(P, A) = C_2 I_{PSA} f_D(A) f_L(P) ,
\]

where \(I_{PSA}\), given by equation (3.10), is the intensity through an ideal PSA ellipsometer, and \(C_2\) is a constant. The effects of the source and detector optics are given by the functions \(f_L(P)\) and \(f_D(A)\) as

\[
f_L(P) = \left[ 1 + \frac{l_{2,1}}{l_{1,1}} \cos(2P) + \frac{l_{3,1}}{l_{1,1}} \sin(2P) \right]
\]

and

\[
f_D(A) = \left[ 1 + \frac{d_{1,2}}{d_{1,1}} \cos(2A) + \frac{d_{1,3}}{d_{1,1}} \sin(2A) \right] .
\]

Note that \(l_{2,1}/l_{1,1}\) and \(l_{3,1}/l_{1,1}\) can be written as \(l_1\) and \(l_2\), respectively, as shown in equations (3.20) and (3.21). It can be seen from equations (3.24)–(3.26) that
Figure 3.4: Source parameters, $l_1$ and $l_2$ as functions of the wavelength.
if the analyzer setting \((A)\) is held fixed, the term involving \(d_{ij}\) is constant and can be grouped with \(C_2\). Therefore, as stated previously, the \([D]\) matrix does not influence measurements from a PSA ellipsometer while the analyzer setting is held fixed.

Equation (3.23) can also be written in terms of a truncated Fourier series (equation (3.3)), with the experimental Fourier coefficients given as

\[
a'_{2} = \frac{2(a_2 + l_1)}{2 + l_1 a_2 + l_2 b_2}, \tag{3.27}
\]

\[
b'_{2} = \frac{2(b_2 + l_2)}{2 + l_1 a_2 + l_2 b_2}, \tag{3.28}
\]

\[
a'_{4} = \frac{1}{2}(l_1 a_2 - l_2 b_2) \tag{3.29}
\]

and

\[
b'_{4} = \frac{1}{2}(l_1 b_2 + l_2 a_2) \tag{3.30}
\]

where \(a_2\) and \(b_2\) are the Fourier coefficients of the ideal ellipsometer system given by equations (3.17) and (3.18).

In order to calculate the ellipsometric parameters \((\rho\) and \(\Delta)\) from equations (3.27)–(3.30), the ideal Fourier coefficients \((a_2\) and \(b_2\)) must first be calculated. In terms of the experimental Fourier coefficients \((a'_2\) and \(b'_2\)), the ideal Fourier coefficients may be written as

\[
b_2 = \frac{2(b'_2 - l_2)(2 - a'_2 l_1) + 2b'_1 l_1(a'_2 - l_2)}{(2 - b'_2 l_2)(2 - a'_2 l_1) - 2a'_2 b'_1 l_1 l_2}, \tag{3.31}
\]

and

\[
a_2 = \frac{a'_2 (2 + l_2 b_2) - 2l_1}{2 - a'_2 l_1}. \tag{3.32}
\]
The results shown in equations (3.27)-(3.32) can be further generalized by considering a general optical system located between the analyzer ([A]) and polarizer ([P]), instead of only a reflecting surface ([S]). If this general optical system has a Mueller matrix [T], the Mueller matrix of the entire system will be given as

\[
[M] = [D][A][T][P][L] .
\]  

(3.33)

The intensity of the beam reaching the detector (equal to the (1,1) element of matrix [M] in equation (3.33)) is given as

\[
I = C_3 \left[ [A][T][P] \right]_{1,1} f_D(A) f_L(P) ,
\]

(3.34)

where \( C_3 \) is a constant and \( \left[ [A][T][P] \right]_{1,1} \) represents the beam intensity if the source and detector optics were considered ideal (i.e. \([L]\) and \([D]\) equal to the identity matrix). The functions \( f_L(P) \) and \( f_D(A) \) are given by equations (3.25)-(3.26).

Therefore, it is seen that the source and detector optics influence the beam intensity of a \([P][T][A]\) ellipsometer system in the same manner, regardless of the nature of matrix \([T]\). This means that equations (3.27)-(3.32) are generally valid because the source/detector perturbed Fourier coefficients (\( a'_2 \) and \( b'_2 \)) are given in terms of the ideal Fourier coefficients (\( a_2 \) and \( b_2 \)). It is shown in Appendix C that \( \left[ [A][T][P] \right]_{1,1} \) is a sinusoidally varying function of both \( A \) and \( P \), with frequencies of \( 2A \) and \( 2P \).
3.5 Birefringent Windows

In the ideal case, the windows would have no effect on beam polarization, with their Mueller matrices \([W_1]\) and \([W_2]\) being given as some multiple of the identity matrix. In the practical sense, the windows do affect beam polarization. Transparent windows such as those used in the present study can be modelled as small wave retardation plates (SWRP) \([33, 56-57]\), with this small wave retardation being caused by birefringence. The birefringence may be either natural birefringence due to the ordered crystal structure of the window material or stress birefringence due to differences in the principal stresses \([58]\). The stress may be an internal stress caused by the manufacturing process or it may be caused by external forces, such as those induced by mounting fixtures. The window material used in this experimental setup (Figure 3.1) is fused quartz, which possesses no ordered crystal structure. This material is also guaranteed by the manufacturer to have been annealed to a low level of birefringence \((< 10 \text{ millimicrons/cm} [59])\). Therefore, it can be concluded that the birefringence in the windows are caused by stresses in the material, with the internal stresses being less significant that the stresses caused by external loads.

3.5.1 Window Matrices

As previously mentioned, the cell windows have been modelled using the SWRP approximation \([33, 56-57]\). The Mueller matrix of the entrance window \((W_1)\) is
that of a linear retarder (see Appendix A), with the retardation being considered small. Therefore, matrix \([W_1]\) can be written as [56]

\[
[W_1] = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & -\alpha_1 \\
0 & 0 & 1 & \beta_1 \\
0 & \alpha_1 & -\beta_1 & 1
\end{bmatrix},
\]

(3.35)

where

\[
\alpha_1 \approx \sin(2\gamma_1)\delta_1
\]

(3.36)

and

\[
\beta_1 \approx \cos(2\gamma_1)\delta_1.
\]

(3.37)

The terms \(\gamma_1\) and \(\delta_1\) are defined in the context of a linear retarder as shown in Appendix A. Similarly, matrix \([W_2]\) can be written as

\[
[W_2] = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & 1 & 0 & -\alpha_2 \\
0 & 0 & 1 & \beta_2 \\
0 & \alpha_2 & -\beta_2 & 1
\end{bmatrix},
\]

(3.38)

where

\[
\alpha_2 \approx \sin(2\gamma_2)\delta_2
\]

(3.39)

and

\[
\beta_2 \approx \cos(2\gamma_2)\delta_2.
\]

(3.40)

In equations (3.36)-(3.37) and (3.39)-(3.40), \(\delta\) refers to the retardation of the window and \(\gamma\) refers to the orientation of the fast axis (axis of least retardation). If the window is considered to be in a condition of plane stress, the difference in refractive indices (\(\Delta n\)) along the principal stress axes is directly proportional to
the difference in principal stresses, with the constant of proportionality known as
the stress optic coefficient \cite{58}. The retardation, \( \delta \), is the amount the component
polarized along the slow axis (largest refractive index) is retarded relative to the
component polarized along the fast axis (smallest refractive index). Since the
electric field amplitude of a polarized beam is represented as a sine wave of
frequency \( \omega = 2\pi/\lambda \), the retardation represents a change in the relative phase of
the two components of polarization, and is given as \cite{41}

\[
\delta = \frac{2\pi (\Delta n) d}{\lambda}, \quad (3.41)
\]

where \( \Delta n \) is the refractive index difference along the principal stress axes, \( d \) is
the thickness of the window, and \( \lambda \) is the vacuum wavelength of light. For a
given stress level, \( \Delta n \) is a fixed constant (at a particular wavelength) and the
retardation can be written as

\[
\delta = \frac{C_1}{\lambda}, \quad (3.42)
\]

where \( C_1 \) is a constant containing the stress optic coefficient. If the stress optic
coefficient is independent of wavelength (i.e. shows no dispersion), the retardation (\( \delta \)) is inversely proportional to wavelength (\( \lambda \)). Practically speaking, most
materials do exhibit some dispersion of the stress optic coefficient, and therefore,
\( \delta \) is not exactly inversely proportional to \( \lambda \). Note that since the birefringence pa-
rameters of the windows (\( \alpha_1, \beta_1, \alpha_2, \) and \( \beta_2 \)) are proportional to the retardation
(see equations (3.36)–(3.37) and (3.39)–(3.40)), the birefringence parameters will
vary with wavelength in the same manner as the retardation.
3.5.2 Window Effects

If the windows of the ellipsometer system are modelled as small wave retardation plates (SWRP; see equations (3.35)-(3.40)), the Mueller matrix of the entire system can be written as

\[ [M] = [A][W_2][S][W_1][P], \]  

(3.43)

where \([W_1]\) and \([W_2]\) are given by equations (3.35) and (3.38). Since it was stated in the previous section that the intensity of any general \([A][T][P]\) optical system varies sinusoidally with respect to \(A\) and \(P\) (with frequencies of 2\(A\) and 2\(P\)), a complete description of the beam intensity can be given by simply describing the second Fourier coefficients, \(a_2\) and \(b_2\). The Fourier coefficients for the system described by equation (3.43) are given by

\[ a_2 = \frac{\rho^2 - \tan^2(A) + \alpha_1 2 \rho \sin(\Delta) \tan(A)}{\rho^2 + \tan^2(A)} \]  

(3.44)

and

\[ b_2 = \frac{2 \rho \cos(\Delta) \tan(A) + 2 \rho \sin(\Delta) \times \left[ \frac{a_1}{2} (1 - \tan^2(A)) - (\beta_2 + \beta_1) \tan(A) \right]}{\rho^2 + \tan^2(A)}, \]  

(3.45)

where \(\alpha_1, \beta_1, \alpha_2, \) and \(\beta_2\) are the birefringence parameters of the entrance (subscript 1) and exit (subscript 2) windows, \(\rho\) and \(\Delta\) are the ellipsometric parameters of the sample, and \(A\) is the analyzer azimuth setting. If the birefringence parameters of the windows are assumed known, equations (3.44) and (3.45) can be solved for \(\rho\) and \(\Delta\) in terms of the Fourier coefficients. These equations are
non-linear coupled equations and must be solved numerically. The two equations may be reduced to one equation by solving equation (3.44) for $\rho$ in terms of $\Delta$ as

$$\rho = \tan (A) \frac{-\alpha_1 \sin (\Delta) + \sqrt{\alpha_2^2 \sin^2 (\Delta) + 1 - a_2^2}}{1 - a_2}.$$  

(3.46)

This solution for $\rho$ can then be substituted into equation (3.45), yielding a transcendental equation with $\Delta$ as the only unknown. The solution can be obtained using a standard root solving method, such as the secant method.

It is to be noted that the Fourier coefficients appearing in equations (3.44)-(3.46) are the coefficients of the $[A][W_2][S][W_1][P]$ optical system, and that the effect of source optics (matrix $[L]$) have not been considered. Thus the Fourier coefficients must be corrected for source optics effects as well as window effects using equations (3.31) and (3.32).

### 3.5.3 Calculation of the Birefringence Parameters

In order to utilize equations (3.44)-(3.46), the birefringence parameters of the windows ($\alpha_1$, $\beta_1$, $\alpha_2$, $\beta_2$) must be known at the wavelength of interest. The birefringence parameters can be calculated using equations (3.44)-(3.46) if the ellipsometric parameters, $\rho$ and $\Delta$, are known. The ellipsometric parameters can be found by performing measurements with the windows removed. The birefringence parameters are more easily calculated by considering one window at a time. If the exit window parameters ($\alpha_2$, $\beta_2$) are known, the entrance window
parameters are given as

\[ \alpha_1 = \frac{\rho^2 (a_2 - 1) + \tan^2 (A) (a_2 + 1)}{2 \rho \sin (\Delta) \tan (A)} \quad (3.47) \]

and

\[ \beta_1 = \frac{-b_2 [\rho^2 + \tan^2 (A)] + 2 \rho \cos (\Delta) \tan (A)}{2 \rho \sin (\Delta) \tan (A)} + \frac{\alpha_2 [1 - \tan^2 (A)]}{2 \tan (A)} - \beta_2 . \quad (3.48) \]

The exit window parameters \((\alpha_2, \beta_2)\) can be found by performing measurements with the entrance window \((W_1)\) removed, leaving only the exit window \((W_2)\) in position. From equations \((3.44)\) and \((3.45)\), it is seen that \(\alpha_2\) and \(\beta_2\) are only dependent upon the Fourier sine coefficient, \(b_2\). Therefore, the exit window parameters cannot be found from a single measurement of the Fourier coefficients.

In order to calculate both \(\alpha_2\) and \(\beta_2\), the Fourier coefficients must be measured for two different analyzer azimuths, \(A_1\) and \(A_2\). The exit window parameters are given as

\[ \beta_2 = \frac{\left[1 - \tan^2 (A_1)\right] \times \left[b_{2B} (\rho^2 + \tan^2 (A_2)) - 2 \rho \cos (\Delta) \tan (A_2)\right]}{2 \rho \sin (\Delta) \left[\tan (A_1) - \left[1 - \tan^2 (A_1)\right] \tan (A_2)\right]} - \frac{b_{2A} (\rho^2 + \tan^2 (A_1)) - 2 \rho \cos (\Delta) \tan (A_1)}{2 \rho \sin (\Delta) \left[\tan (A_1) - \left[1 - \tan^2 (A_1)\right] \tan (A_2)\right]} \quad (3.49) \]

and

\[ \alpha_2 = \frac{b_{2A} [\rho^2 + \tan^2 (A_1)] - 2 \rho \cos (\Delta) \tan (A_1)}{2 \rho \sin (\Delta) [1 - \tan^2 (A_1)]} + \frac{\beta_2 \tan (A_1)}{1 - \tan^2 (A_1)} , \quad (3.50) \]

where \(b_{2A}\) and \(b_{2B}\) are the second Fourier sine coefficients measured at analyzer azimuths \(A_1\) and \(A_2\), respectively.
3.6 Solution Methodology

The preceding sections have presented equations whereby the beam intensity through an ellipsometer system could be measured in order to calculate the optical properties of a bulk sample. The procedure is summarized as follows:

1. Find the ellipsometric parameters ($\rho$ and $\Delta$) of the sample with both cell windows removed.

2. With only the exit window ($W_2$) in position, find the birefringence parameters of the exit window ($\alpha_2$ and $\beta_2$).

3. With both windows in position, find the birefringence parameters of the entrance window ($\alpha_1$ and $\beta_1$).

4. With both windows in position, find the ellipsometric parameters ($\rho$ and $\Delta$) and the complex refractive index ($n$ and $k$) of the sample for different sample temperatures. The window parameters ($\alpha_1$, $\beta_1$, $\alpha_2$, and $\beta_2$) and source parameters ($l_1$ and $l_2$) are constant as the sample temperature is varied.

The steps for this procedure are shown in a flowchart, Figure 3.5. As seen in this flowchart, the first step of each procedure indicates that $I(P)$ is to be measured at a given analyzer azimuth. This measurement involves measuring the intensity over a full revolution of the polarizer for some interval of the polarizer azimuth setting.
I. Windows: None

Given: \( l_1, l_2 \)

Find: \( \rho, \Delta \)

\[
\begin{align*}
I(P) \quad A = 35^\circ \quad (3.4) - (3.8) & \quad a'_2, b'_2 \quad (3.31) - (3.32) & \quad a_2, b_2 \quad (3.17) - (3.18) & \quad \rho, \Delta
\end{align*}
\]

II. Windows: \( W_2 \)

Given: \( l_1, l_2, \rho, \Delta \)

Find: \( \alpha_2, \beta_2 \)

\[
\begin{align*}
I(P) \quad A_1 = 30^\circ \quad (3.4) - (3.8) & \quad a'_{2A}, b'_{2A} \quad (3.31) - (3.32) & \quad a_{2A}, b_{2A} \quad (3.49) - (3.50) & \quad \alpha_2, \beta_2
\end{align*}
\]

\[
\begin{align*}
I(P) \quad A_2 = 40^\circ \quad (3.4) - (3.8) & \quad a'_{2B}, b'_{2B} \quad (3.31) - (3.32) & \quad a_{2B}, b_{2B}
\end{align*}
\]

III. Windows: \( W_1, W_2 \)

Given: \( l_1, l_2, \rho, \Delta, \alpha_2, \beta_2 \)

Find: \( \alpha_1, \beta_1 \)

\[
\begin{align*}
I(P) \quad A = 35^\circ \quad (3.4) - (3.8) & \quad a'_2, b'_2 \quad (3.31) - (3.32) & \quad a_2, b_2 \quad (3.47) - (3.48) & \quad \alpha_1, \beta_1
\end{align*}
\]

IV. Windows: \( W_1, W_2 \)

Given: \( l_1, l_2, \alpha_1, \beta_1, \alpha_2, \beta_2 \)

Find: \( \rho, \Delta, n, k \)

\[
\begin{align*}
I(P) \quad A = 35^\circ \quad (3.4) - (3.8) & \quad a'_2, b'_2 \quad (3.31) - (3.32) & \quad a_2, b_2 \quad (3.44) - (3.46) & \quad \rho, \Delta \quad (2.60) - (2.63) & \quad n, k
\end{align*}
\]

Figure 3.5: Flowchart of solution methodology. Numbers in parentheses signify equation numbers used in data inversion.
Chapter 4

Surface Roughness Effects

Up to this point, only planar, perfectly smooth surfaces have been considered when analyzing the reflection of light from a surface. Considering a surface to be perfectly smooth is an idealization, since all real surfaces are rough to some degree. Qualitatively, a surface is considered to be smooth if the roughness of the surface is small compared to the wavelength of the incident radiation. This chapter will consider the effects of surface roughness on the reflection of light from a surface and it will also consider the effects of surface roughness on the determination of the refractive indices utilizing the reflection technique. The bulk of this chapter is taken from a journal article by Stagg and Charalampopoulos [40] describing the effects of surface roughness on the interpretation of data gathered by the reflection technique. Although ellipsometry is the optical technique chosen for this study, an analysis of the reflection technique will allow some important conclusions.
This chapter will present a review of the existing literature on the reflection technique, followed by a description of the reflectivity of rough surfaces. The reflectometer system utilized is described and the experimental results are presented. The mathematical models which describe surface roughness are discussed, and finally, conclusions are drawn about this work and its relevance to the ellipsometry technique. Note that in this chapter, the symbol $\rho$ is used to denote the bidirectional reflectivity of a rough surface having infinite conductivity, or equivalently, the roughness factor of a surface having finite conductivity. This term should not be confused with the first ellipsometric parameter of a sample. In this chapter, $\rho$ will always signify roughness factor unless it is specifically stated to mean ellipsometric parameter.

### 4.1 Introduction

The reflection technique has been proven to be a valuable tool for the determination of the optical properties of materials. It has been used for studying the refractive indices of metals (see for example, [60–61]) carbonaceous materials [2–3,6,9–10,62–66] as well as glasses [67]. In particular, the reflection method is especially suitable for absorbing solids for which the preparation of thin specimens required for transmission measurements is difficult [68]. The appropriate combination of reflection measurements that should be used in order to surmount some of the difficulties associated with the reflection technique was originally proposed by Avery [69]. Specifically, the ratio of the reflection coefficients polarized
in the direction parallel \((R_{||})\) and perpendicular \((R_{\perp})\) to the plane of incidence was proposed as the appropriate relation for data inversion. Several other investigators \([51,60,70]\) have proposed suitable sets of reflection measurements and data inversion schemes to determine the optical constants. In all cases the Fresnel equations were used to calculate the reflection coefficients in both planes of polarization. However, as has been pointed out by Janzen \([16]\), use of the Fresnel equations require that the reflection surface be catoptrically flat. Under this condition, the specularity index of the surface, defined as the ratio of the square of the perpendicular component of the reflected radiation to the parallel component evaluated at an angle of incidence of 45 degrees, should be equal to one. The same criterion was used by Felske and coworkers \([9]\) in determining the applicability of the Fresnel equations for inverting angular reflection data in both planes of polarization. A more detailed review of the sensitivity of the reflection method to the instrument characteristics, such as polarizer leakage, was presented recently by Stagg and Charalampopoulos \([39]\). In addition, a method was developed which allows corrections of the reflectivity measurements when the extinction ratio of the polarizing film is larger than \(10^{-3}\). Nevertheless, the effects of surface roughness on the inferred optical properties have not been assessed.

In this study, angular reflection measurements were carried out on a carbon rod with different roughness levels at a wavelength of 3.5 microns. The different roughness levels were obtained by sanding the carbon surface with emery paper
of variable grit size, ranging from 320 to 4,000. The corresponding specularity indices varied in the range 0.076 to 0.99. It is shown that the inferred real and imaginary parts of the index may be in error by 30 and 55 percent or more when the surface is inadequately prepared and the inappropriate data inversion scheme is employed. In addition, it is demonstrated that when the ratio of the angular reflectances in both planes of polarization are employed in the data inversion, the optical properties can be accurately inferred even if the reflecting surface is moderately rough. Results are presented for the roughness factors of the surface as a function of the angle of incidence and the potential for obtaining the root mean square roughness ($\sigma$) and the surface correlation length ($\alpha$) from measurements of the specularity index is discussed.

4.2 Reflectivity of Rough Surfaces

The effects of surface roughness on the measured reflectivities have been investigated both theoretically and experimentally. The mathematical models that describe the reflectivity from a rough surface are derived from the Kirchoff diffraction theory [71–72] assuming a statistically random surface and a material with infinite conductivity. The assumption of infinite conductivity facilitates the reduction of the pertinent equations to forms that yield workable solutions. Since a smooth material with infinite conductivity has a reflectivity of one, the mathematical models predict the deviation of the reflectivity from unity due to the diffuse nature of the surface. The reflectivity of a rough surface with infinite
conductivity can be predicted by the complete models proposed by Davies [71] and Beckmann and Spizzichino [72]. Both models require knowledge of two parameters in order to describe the surface roughness: the root mean square roughness ($\sigma$) and the correlation length ($\alpha$) (see Houchens and Hering [73]). Davies' model is restricted to small slopes and to the limiting cases of a very small and very large optical roughness. For a material with infinite conductivity Davies' model predicts the bidirectional reflectivity as

$$\rho_D = e^{-f} + f \pi \left(\frac{\alpha}{\lambda}\right)^2 \cos(\theta) \Delta \omega,$$  
(4.1)

where the first and second term represent the specular and diffuse component of the reflected radiation, respectively. The term $\Delta \omega$ represents the solid angle of the detection optics, which is defined by the monochromator slit opening $A_s$, the distance from the reflection surface $R$, and the angle of incidence $\theta$ ($\Delta \omega = A_s \cos(\theta)/R^2$). It is noted that the angle of incidence, $\theta$, is measured from the normal of the mean surface plane of the sample. The factor $f$ is related to the ratio $\sigma/\lambda$ (where $\lambda$ is the wavelength of the incident radiation) and the angle of reflection ($\theta$) by the expression

$$f = \left[4\pi \cos(\theta) \frac{\sigma}{\lambda}\right]^2.$$  
(4.2)

For a broader range of roughness Houchens and Hering [73] suggest a more simplified relation for the reflectivity of the rough surface based on the Beckmann
and Spizzichino model

\[ \rho_{BS} = e^{-f} \left[ 1 + \pi \left( \frac{\alpha}{\lambda} \right)^2 \cos (\theta) \Delta \omega \sum_{m=1}^{\infty} \frac{f_m}{m \cdot m!} \right]. \]  

(4.3)

It is noted that in both models the assumption is made that the distribution of heights of the surface irregularities is Gaussian about the mean. More details about this assumption are given in Section 4.5. In addition, the autocovariance function of the surface irregularities is also Gaussian with known standard deviation. For slightly rough surfaces of materials with infinite conductivity, both models (equations (4.1) and (4.3)) can be reduced to the specular component alone, which is given by

\[ \rho_s = \exp \left[ - \left( 4\pi \cos (\theta) \frac{\sigma}{\lambda} \right)^2 \right]. \]  

(4.4)

In the case of a material with finite conductivity (see for example [72,74–75]), the angular reflectance of a rough surface may be expressed as the product of a surface roughness dependent quantity and a material dependent quantity, namely:

\[ R(\tilde{m}, \theta, \sigma/\lambda) = \rho(\theta, \sigma/\lambda) \cdot R_0(\tilde{m}, \theta), \]  

(4.5)

where \( \rho(\theta, \sigma/\lambda) \) may be given in the general case by equation (4.1) or (4.3) and \( R_0(\tilde{m}, \theta) \) is the reflectivity of a smooth surface with the same refractive index \( \tilde{m} \) as the surface of interest. According to Beckmann and Spizzichino [72], the function \( \rho(\theta, \sigma/\lambda) \) represents, in essence, a mean value of the reflection coefficient over the surface. The reflectivity \( R_0(\tilde{m}, \theta) \) can be calculated from the Fresnel equations once the complex refractive index \( \tilde{m} = n - ik \) is known. Since in the
reflection technique, knowledge of both components of polarization is needed, it is desirable to apply equation (4.5) in both planes of polarization. In this regard, Hensler [76] has demonstrated that the roughness factor $\rho(\theta, \sigma/\lambda)$ is the same in both the vertical and horizontal planes of polarization. Under this condition, equation (4.5) yields for the reflection coefficients

$$R_\parallel = \rho R_{0,\parallel}$$  \hspace{1cm} (4.6)

and

$$R_\perp = \rho R_{0,\perp}.$$  \hspace{1cm} (4.7)

The subscripts $\parallel$ and $\perp$ indicate polarization parallel and perpendicular to the plane of incidence. Ratioing equations (4.6) and (4.7) yields

$$\frac{R_\parallel}{R_\perp} = \frac{R_{0,\parallel}}{R_{0,\perp}}.$$  \hspace{1cm} (4.8)

Thus, the reflectance ratio from a rough surface is the same as that from a smooth surface of the same material. It is to be noted that equation (4.8) is independent of the statistical nature of the roughness distribution function. This implies that the complex refractive index ($\tilde{n} = n - ik$) of a rough surface can be determined by measuring the reflectance ratio at a minimum of two different angles of incidence and solving simultaneously the Fresnel equations.

The optical quality of a smooth surface can be evaluated by measuring the ratio $R_\perp^2/R_\parallel$ at the angle of incidence of 45 degrees, since from the Fresnel
equations, it can be shown that

\[
\frac{R_{O,\perp}^2}{R_{O,\parallel}} = 1.0 . \tag{4.9}
\]

This quantity is referred to as the specularity index and is independent of the refractive index of the material. Thus, measurement of the deviation of the specularity index from unity provides an indicator of the degree of surface roughness.

For a slightly rough surface, an analogous quantity can be introduced for the specular character of the surface. Combining equations (4.4), (4.6) - (4.7) and (4.9) and noting that \( \frac{R_{\perp}^2}{R_{\parallel}} = \rho R_{O,\perp}^2 / R_{O,\parallel} \) the specularity index for a slightly rough surface may be written as

\[
\frac{R_{\perp}^2}{R_{\parallel}} \mid_{\theta=45^\circ} = \exp \left[ \frac{-8\pi^2 \sigma^2}{\lambda^2} \right] = SI . \tag{4.10}
\]

Equation (4.10) is very important because it provides an optical means of finding the root mean square roughness \( \sigma \) by a simple measurement of the specularity index \( SI \) without knowledge of the refractive index of the sample. This relation possesses the proper limits since as the root mean square roughness, \( \sigma \), approaches zero, the specularity index, \( SI \), approaches one. The experimental approach and the method of analysis used in this study in order to determine the refractive indices of a non-specular surface are presented below.
4.3 Experimental System

The effects of surface roughness on the inferred optical constants were assessed by measuring the reflectances \( R_\parallel \) and \( R_\perp \) of a carbon rod with various degrees of roughness, at a fixed wavelength of the incident radiation \( \lambda = 3.5 \) microns. For each roughness level, the reflectances \( R_\parallel \) and \( R_\perp \) were measured over the angular range 25 to 75 degrees at 0.5 degree intervals. The surface roughness of the rod was varied by sanding with emery paper of variable grit (320 grit to 4,000 grit) and the use of a polishing cloth. The carbon rod, 99.999% pure, has a diameter of 1.0 cm. The reflectance measurements were carried out in a reflectometer system shown in Figure 4.1.

The reflectometer consists of a fixed platform and two rotating bases: the inner base supports the sample holder (SH) whereas the outer base (RB) supports the light source and focusing optics. The light source rotates with twice the speed of the sample holder. As a result, the incident light beam on the front surface of the sample is reflected along the same direction for all angles of incidence. This characteristic allows for the collection optics to be mounted at a fixed position on the goniometer base and renders the measurements less cumbersome. The light source consists of a xenon arc lamp and is mounted on an air cooled monochromator illuminator housing, ORIEL model 68700. The light is focused by a rotary concave mirror (RCM) at a distance 63.5mm in front of the exit port of the housing. A set of iris diaphragms are mounted after the
Figure 4.1: Reflectometer System: LS (light source), RCM (rotatable concave mirror, f.l. = 63.5 mm), I (iris), LC (light chopper), P1 (plane mirror, dia. = 50 mm), C1 (spherical mirror, f.l. = 150 mm, dia. = 50 mm), SH (sample holder), P2 (plane mirror, dia. = 50 mm), C2 (spherical mirror, f.l. = 200 mm, dia. = 50 mm), RB (rotatable base), P (polarizer), MS (monochromator slit), M (grating monochromator), F (cut on wavelength filter), D (detector).
exit port to provide control of the beam width. A light chopper, EG&G model 196, modulates the incident light at a frequency of 500 Hz. The output signal from the light chopper serves as a reference input to the lock in amplifier that filters out the unwanted noisy component of the signal. The chopped radiation is focused by the mirrors P1 and C1 on the center of the sample surface which is held in vertical position by the sample holder (SH). The reflected beam from the surface is directed by the flat mirror P2 and concave mirror C2 which focuses the beam on the entrance slit of the monochromator. The state of polarization of the reflected beam was defined by a gold wire grid polarizer on silver bromide substrate, PERKIN ELMER model 186-0240. At the wavelength of 3.5 microns, the extinction ratio of the polarizer used is $4.55 \times 10^{-3}$. The reflection measurements at both states of polarization were corrected using this value of the extinction ratio and the method developed recently by Stagg and Charalampopoulos [39]. The polarizer was mounted in front of the slit of the monochromator normal to the incoming radiation on a specially designed fixture that allowed 90 degree rotation with respect to the vertical polarization orientation of the reflected radiation from the sample surface. The reflected radiation was dispersed by an ORIEL monochromator model 77250 equipped with an electrically driven wavelength readout at 1.617 nanometers per second. The dispersed light signal was detected by an Indium Antimonide infrared detector and subsequently filtered by a lock-in amplifier (EG&G model 5207).
4.4 Results

The data were inverted for the real \((n)\) and imaginary \((k)\) parts of the refractive index by an optimization procedure with the objective function defined as

\[
F = \sum_{i=1}^{N} \left[ G_{th,i} - G_{exp,i} \right]^2 ,
\]

(4.11)

where \(G_{th,i}\) and \(G_{exp,i}\) are functions of the theoretical and measured reflectivities, respectively and \(N\) is the number of data points \((N = 101\) in this study). For optically smooth surfaces, it is possible to use a variety of forms of the function \(G\). A form that has been found to yield good results for smooth materials is \(G = R_{\parallel}\). For the rough surfaces \((SI < 1.00)\) used in this study, the most suitable form for the data inversion was found to be

\[
G = \frac{R_{\parallel}}{R_{\perp}} .
\]

(4.12)

The upper graphs in Figures 4.2-4.5 show the measured values of the reflectivity \((R_{\parallel}, R_{\perp})\) at the wavelength of 3.5 microns along with the calculated values based on the Fresnel equations. As it may be seen when the specularity index increases from 0.076 to 0.99, the agreement between the Fresnel equations and the measured reflectivities becomes progressively better. The lower graphs of Figures 4.2-4.5 show that when the measured reflectance ratio \((R_{\parallel}/R_{\perp})\) is compared with the predicted values the agreement is excellent regardless of the degree of surface roughness. Thus, as the surface becomes optically smooth, it can be seen that the individual reflectivities as well as the reflectance ratio conform to the
Figure 4.2: Reflectivities (upper graph) and reflectivity ratio (lower graph) versus angle of incidence for the carbon rod surface with a specularity index $SI = 0.076$. Points are experimental data and solid lines correspond to the predictions of the Fresnel equations. The inferred refractive index is $\tilde{m} = 3.708 - 1.598i$. 
Figure 4.3: Reflectivities (upper graph) and reflectivity ratio (lower graph) versus angle of incidence for the carbon rod surface with a specularity index $SI = 0.376$. Points are experimental data and solid lines correspond to the predictions of the Fresnel equations. The inferred refractive index is $\tilde{m} = 3.730 - 1.564i$. 
Figure 4.4: Reflectivities (upper graph) and reflectivity ratio (lower graph) versus angle of incidence for the carbon rod surface with a specularity index $SI = 0.739$. Points are experimental data and solid lines correspond to the predictions of the Fresnel equations. The inferred refractive index is $\tilde{n} = 3.736 - 1.663i$. 
Figure 4.5: Reflectivities (upper graph) and reflectivity ratio (lower graph) versus angle of incidence for the carbon rod surface with a specularity index $SI = 0.99$. Points are experimental data and solid lines correspond to the predictions of the Fresnel equations. The inferred refractive index is $\tilde{n} = 3.860 - 1.543i$. 
Fresnel theory. It is also noted that the effects of surface roughness on reflectivity decrease as the angle of incidence increases. This trend is consistent with the prediction of equation (4.4).

At this point it should be noted that since the complex refractive index is a material property, it should not depend on the degree of surface roughness. The present results show that this is indeed the case when the proper function (see equation 4.12) is used for data inversion. Specifically, as it may be seen from Figures 4.6–4.7 when the reflectance ratio is used, the inferred refractive indices are essentially independent of the specularity index. On the other hand, when the parallel component of the polarization ($R_{||}$) is used, the resulting indices depend heavily on the degree of the surface roughness. However, as the surface becomes smoother ($SI$ approaching 1.0), both inversion schemes yield the same results. A more detailed comparison of the inferred refractive indices for the values of the specularity index in the range 0.076 to 0.99 is shown in Table 4.1. These values are compared with the indices corresponding to $SI = 0.99$. As it may be seen, the average percent differences between the values of $n$ and $k$ corresponding to a specularity index of 0.99 and other values is 2.9 and 5.0, respectively. These results emphasize the need for the proper scheme of data inversion and, in addition, demonstrate that the material surface does not have to be catoptrically flat in order to determine the refractive indices by the reflection method. As a matter of interest, it is noted that a sample which appears to be
Figure 4.6: Real part of the refractive index as a function of the specularity index of the carbon rod surface inferred from the inversion of the reflectance ratio (○) and from the parallel component of the reflectivity (■).
Figure 4.7: Imaginary part of the refractive index as a function of the specularity index of the carbon rod surface inferred from the inversion of the reflectance ratio (○) and from the parallel component of the reflectivity (■).
Table 4.1: Complex refractive index at various values of specularity index compared to the refractive index at $SI = 0.99$.

<table>
<thead>
<tr>
<th>$SI$</th>
<th>$n$</th>
<th>$k$</th>
<th>$n/n_{0.99}$</th>
<th>$k/k_{0.99}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.076</td>
<td>3.708</td>
<td>1.598</td>
<td>0.957 (4.3)*</td>
<td>1.042 (4.2)</td>
</tr>
<tr>
<td>0.205</td>
<td>3.678</td>
<td>1.549</td>
<td>0.949 (5.1)</td>
<td>1.010 (1.0)</td>
</tr>
<tr>
<td>0.364</td>
<td>3.826</td>
<td>1.420</td>
<td>0.987 (1.3)</td>
<td>0.926 (7.4)</td>
</tr>
<tr>
<td>0.376</td>
<td>3.753</td>
<td>1.574</td>
<td>0.969 (3.1)</td>
<td>1.026 (2.6)</td>
</tr>
<tr>
<td>0.510</td>
<td>3.769</td>
<td>1.574</td>
<td>0.973 (2.7)</td>
<td>1.026 (2.6)</td>
</tr>
<tr>
<td>0.591</td>
<td>3.733</td>
<td>1.652</td>
<td>0.976 (2.4)</td>
<td>1.077 (7.7)</td>
</tr>
<tr>
<td>0.739</td>
<td>3.736</td>
<td>1.663</td>
<td>0.964 (3.6)</td>
<td>1.084 (8.4)</td>
</tr>
<tr>
<td>0.871</td>
<td>3.726</td>
<td>1.698</td>
<td>0.962 (3.8)</td>
<td>1.107 (10.7)</td>
</tr>
<tr>
<td>0.952</td>
<td>3.801</td>
<td>1.537</td>
<td>0.981 (1.9)</td>
<td>1.002 (0.2)</td>
</tr>
<tr>
<td>0.982</td>
<td>3.843</td>
<td>1.615</td>
<td>0.992 (0.8)</td>
<td>1.053 (5.3)</td>
</tr>
<tr>
<td>0.990</td>
<td>3.875</td>
<td>1.534</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Average percent differences: 2.9 5.0

* Numbers in parenthesis represent percent differences between the values of $n$ and $k$ at a value of $SI = 0.99$ and other values.

relatively smooth to the naked eye may have a specularity index as low as 0.8 at a wavelength of 3.5 microns. These values correspond to a root mean square roughness to wavelength ratio ($\sigma/\lambda$) of 0.053 and result in a 30% error in the real part of the index when the individual component of polarization ($R_{||}$) is used to invert the data. The same surface would possess an even lower specularity index at smaller wavelengths and will yield a much larger error in the optical properties when a function other than the reflectivity ratio is used for data inversion.
Although no upper limit was placed on the surface roughness when using this technique, it will be increasingly more difficult to measure the reflectance as the surface roughness increases. This is because the specular component of the radiation will not be large enough to yield an adequate signal to noise ratio. In this study the measurements were limited to specularity index of 0.07. It is noted, however, that as long as the reflectivity can be measured, the determination of the refractive index of a material with a moderately rough surface is possible.

4.5 Discussion of the Mathematical Models Describing Surface Roughness Effects

Since the roughness effects are important in determining the spectral radiative properties of material surfaces, it is appropriate to assess the relation of the roughness factor $\rho$ to the roughness parameters $(\sigma/\lambda)$ and $(\alpha/\lambda)^2$ based on the experimental measurements. At this point it should be mentioned that ideally an independent determination of the surface roughness distribution function should be provided. However, the nature of the surface and the degree of roughness levels precludes the use of any mechanical device such as a Talysurf to obtain the distribution function. Nevertheless, it is noted that the emery papers used for polishing the sample surface are manufactured using nearly monosized grain sizes. In addition, the surface roughness distribution of the finished surface is expected to be a close replica of the distribution of the grain sizes that constitute the surface of the polishing paper. Furthermore, it has been found by many
investigators (see for example [36,74,77]) that most randomly generated rough surfaces in practice may be represented by a Gaussian distribution. It is therefore reasonable for the purpose of this first assessment of the roughness factor \( \rho(\theta, \sigma/\lambda) \) in relation to the specularity index \( SI \) and the angle of incidence \( \theta \) to represent the roughness with a Gaussian distribution.

The value of \( \rho \) can be expressed in terms of the measured \( (R_\parallel, R_\perp) \) and computed \( (R_{O,\parallel}, R_{O,\perp}) \) reflectivities by the relation

\[
\rho = \frac{R_\parallel + R_\perp}{R_{O,\parallel} + R_{O,\perp}},
\]

if the optical properties are known. The value of \( \sigma \) used in equation (4.4) is determined by solving equation (4.10) using the measured value of the specularity index. The results of these comparisons are shown in Figure 4.8. It is seen that the agreement between measured and predicted values becomes poorer as the surface roughness increases. More specifically, equation (4.4) will yield unreliable values for the roughness factor \( \rho \) for specularity indices lower that 0.75 or equivalently for values of \( (\sigma/\lambda) \) greater than 0.06. Furthermore, for comparison purposes, the values of the optical roughness parameters \( (\sigma/\lambda) \) and \( ([\alpha/\lambda]^2) \) as predicted by equation (4.1), (4.3), and (4.4) were calculated and listed in Table 4.2. The unknowns \( \sigma \) and \( \alpha \) were obtained by fitting the equations to the measured value of \( \rho \) at the angles of incidence 25 degrees and 45 degrees. Equations (4.1) and (4.3) were then used to compute the values of \( \rho \) over the entire angular range. The comparisons between the data and the predictions of
Figure 4.8: Roughness factor ($\rho$) versus angle of incidence for various values of the specularity index ($SI$). Points are the data and solid lines are predictions by the specular component of reflectance (equation (4.4)).
Figure 4.9: Roughness factor ($\rho$) versus angle of incidence for various values of the specularity index ($SI$). Points are the data and solid lines are predictions by the Davies model (equation (4.1)).
Figure 4.10: Roughness factor ($\rho$) versus angle of incidence for various values of the specularity index ($SI$). Points are the data and solid lines are predictions by the Beckmann–Spizzichino model (equation (4.3)).
Table 4.2: Optical roughness parameters \((\sigma/\lambda)\) and \(\left[\alpha/\lambda\right]^2\) used in equations (4.1), (4.3) and (4.4).

<table>
<thead>
<tr>
<th>SI</th>
<th>Eqn. (4.1)</th>
<th>Eqn. (4.3)</th>
<th>Eqn. (4.4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\sigma/\lambda)</td>
<td>(\alpha/\lambda)^2</td>
<td>(\sigma/\lambda)</td>
</tr>
<tr>
<td>0.076</td>
<td>0.187</td>
<td>1.46</td>
<td>0.208</td>
</tr>
<tr>
<td>0.205</td>
<td>0.147</td>
<td>4.30</td>
<td>0.159</td>
</tr>
<tr>
<td>0.376</td>
<td>0.117</td>
<td>10.6</td>
<td>0.126</td>
</tr>
<tr>
<td>0.591</td>
<td>0.085</td>
<td>13.9</td>
<td>0.088</td>
</tr>
<tr>
<td>0.740</td>
<td>0.063</td>
<td>9.41</td>
<td>0.064</td>
</tr>
<tr>
<td>0.952</td>
<td>0.026</td>
<td>18.8</td>
<td>0.026</td>
</tr>
</tbody>
</table>

equations (4.1), (4.3), and (4.4) are shown in Figures 4.8–4.10. Figures 4.9–4.10 show that the Davies and Beckmann-Spizzichino model provide the same degree of agreement with the experimental data for specularity indices greater than 0.6.

4.6 Conclusion

The effects of moderate surface roughness levels on the determination of the refractive indices were assessed by performing reflection measurements on a surface with variable specularity indices. It was shown that the real and imaginary parts of the complex refractive index of a material with a rough surface can be determined reliably when the ratio of the polarized angular reflectances is known. On the other hand, when only one component of polarized reflectance is used, the inferred indices can be in error by 30 percent or more. Furthermore, an analytical expression was developed that relates the root mean square roughness and
the wavelength of the incident radiation to the measured specularity index. The available analytical models that relate the reflectivity from rough surfaces to the roughness parameters \((\sigma/\lambda)\) and \((\alpha/\lambda)\) were used to compare the angular experimental measurements to the model predictions. The results show that both the Davies and Beckmann–Spizzichino models agree very well with the angular reflectance measurements when the specularity index of the surface is greater than 0.6.

This chapter demonstrates that the reflectance ratio \(R_{\|}/R_{\perp}\) is largely unaffected by the degree of surface roughness. This is because the roughness factor, \(\rho(\theta, \sigma/\lambda)\), was found to be independent of the state of polarization of the incident light, and by ratioing the reflectivities the effects of the roughness factor are cancelled. Since the ellipsometric parameters, \(\rho\) and \(\Delta\), of a surface are found by measuring the intensity ratios of reflected light for various states of polarization, the ratioing process will once again negate the effects of surface roughness. Therefore, the ellipsometric parameters of the surface will be unaffected by the degree of surface roughness. It should be noted that the first ellipsometric parameter, \(\rho\), is related to the reflectance ratio as

\[
\rho^2 = \frac{R_{\|}}{R_{\perp}}.
\]

Nevertheless, it is to be emphasized that many researchers do not agree that the ellipsometric parameters are unaffected by surface roughness. In fact, much work has been performed on the development of models [35,78–79] to predict the
change of the ellipsometric parameters with respect to surface roughness. An overview of the optics of rough surfaces is given by Hunderi [38]. On the other hand, Williams and Aspnes [80] have found a class of rough surfaces that give accurate specular ellipsometric data while being unsuitable for measurements of the individual reflectance components.
Chapter 5

Sensitivity Analysis

The objective of this chapter is to formulate a method of comparing the sensitivity of the photometric ellipsometry technique under different conditions. A technique has been developed by which the sensitivity is assigned a numerical value, thereby allowing a quantitative comparison of the measurement technique under different conditions. This technique of comparing the sensitivity under different conditions based upon a numerical sensitivity value is essentially the same as the concept introduced by Stagg and Charalampopoulos [81] to evaluate the reflection technique. The effect of the angle of incidence and analyzer azimuth on the sensitivity will be discussed. The effect of polarizer quality on the measurement of the refractive index will also be evaluated.

5.1 General Considerations

As mentioned previously, two independent experimental quantities are sufficient to calculate the two components, \( n \) and \( k \), of the complex refractive index of a bare substrate. The two experimental quantities used in this study are the
normalized Fourier coefficients, $a_2$ and $b_2$. It is of interest to determine the overall "sensitivity" of the computed refractive index to the measured Fourier coefficients. Sensitivity refers to the effect errors in the measured Fourier coefficients will have on the accuracy of the computed refractive index. This sensitivity can be greatly affected by the refractive index of the sample, the angle of incidence ($\theta$) utilized, and the azimuthal angle of the analyzer ($A$). A visual indication of sensitivity can be obtained by plotting the Fourier coefficients on an $x$-$y$ axis for lines of constant refractive index, such as the graph shown in Figure 5.1. The grid spacing is an indication of the sensitivity of the technique. A wide grid spacing indicates good sensitivity and a small grid spacing indicates poor sensitivity. It was found from this study that angle of incidence is a very important factor in determining sensitivity for a given material (i.e. for a given $n$ and $k$). Comparing Figures 5.1–5.2, which are plotted on the same scale and under the same conditions except for the angle of incidence ($\theta$), it is seen that the sensitivity of this technique is much better for an angle of incidence of 70 degrees as compared to 45 degrees. It is also seen that the sensitivity is dependent upon the value of the optical properties of the material being measured. The sensitivity of the technique is very poor for materials having either very large or very small values of $k$ and also poor for large values of $n$. 
Figure 5.1: Sensitivity chart of the refractive index with respect to the Fourier coefficients. The angle of incidence is $\theta = 70^\circ$ and the analyzer azimuth is $A = 35^\circ$. 

$1.5 < n < 4.5$

$0 < k < 5$
Figure 5.2: Sensitivity chart of the refractive index with respect to the Fourier coefficients. The angle of incidence is $\theta = 45^\circ$ and the analyzer azimuth is $A = 35^\circ$. 

$\begin{align*}
1.5 < n < 4.5 \\
0 < k < 5
\end{align*}$
5.2 Optimum Conditions

It was stated in the previous section that the grid spacing in Figures 5.1–5.2 is an indication of the sensitivity of the photometric ellipsometry technique. As seen in these figures, the grid spacing depends on the angle of incidence ($\theta$) and the analyzer azimuth ($A$). If conditions of best sensitivity are defined as the angles ($\theta$ and $A$) which yield the maximum grid area, then the optimum value of these angles could be found by a visual inspection of many graphs similar to those in Figures 5.1–5.2. A better approach would be to assign a numerical value to the grid spacing and then maximize this grid spacing with respect to the two input parameters, $\theta$ and $A$. In fact, this problem can be generalized to any problem where two unknowns, say $z_1$ and $z_2$, are calculated from two experimentally measured quantities, say $f_1$ and $f_2$. For this particular problem, the two unknowns, $z_1$ and $z_2$, correspond to the two components of the refractive index, $n$ and $k$, and the two experimentally measured quantities, $f_1$ and $f_2$, correspond to the normalized Fourier coefficients, $a_2$ and $b_2$. An enlarged view of one grid block is shown in Figure 5.3. The area of one grid block may be determined by approximating the shape of the grid block as a parallelogram of lengths $a$ and $b$ with $\gamma$ being the angle between the sides. Thus, the area of one grid block may be written as

$$A = ab|\sin (\gamma)|, \quad (5.1)$$
Figure 5.3: Enlarged view of one grid block.
where the lengths of the sides are given by

\[ a = \left\{ \left[ f_1(x_1 + \Delta x_1, x_2) - f_1(x_1, x_2) \right]^2 + \left[ f_2(x_1 + \Delta x_1, x_2) - f_2(x_1, x_2) \right]^2 \right\}^{1/2} \]

\[ \approx \Delta x_1 \left[ \left( \frac{\partial f_1}{\partial x_1} \right)^2 + \left( \frac{\partial f_2}{\partial x_1} \right)^2 \right]^{1/2} \]  

(5.2)

and

\[ b \approx \Delta x_2 \left[ \left( \frac{\partial f_1}{\partial x_2} \right)^2 + \left( \frac{\partial f_2}{\partial x_2} \right)^2 \right]^{1/2} \]  

(5.3)

From Figure 5.3 it follows that

\[ \gamma = \beta - \alpha , \]  

(5.4)

where

\[ \alpha = \tan^{-1} \left[ \frac{(\partial f_2/\partial x_1)}{(\partial f_1/\partial x_1)} \right] \]  

(5.5)

and

\[ \beta = \tan^{-1} \left[ \frac{(\partial f_2/\partial x_2)}{(\partial f_1/\partial x_2)} \right] . \]  

(5.6)

On the other hand, sin (\(\gamma\)) may be written as

\[ \sin(\gamma) = \left\{ \pm \left[ 1 + \tan^2(\alpha) \right]^{-1/2} \right\} \left\{ \pm \left[ 1 + \tan^2(\beta) \right]^{-1/2} \right\} \{ \tan(\beta) - \tan(\alpha) \} . \]  

(5.7)

Combining equations (5.1)-(5.6) yields for the area of one grid block the relation

\[ A = \Delta x_1 \Delta x_2 \left| \frac{\partial f_1 \partial f_2}{\partial x_1 \partial x_2} - \frac{\partial f_1 \partial f_2}{\partial x_2 \partial x_1} \right| . \]  

(5.8)

A better indicator of the sensitivity may be obtained by defining a normalized area, \(A_N\), as

\[ A_N = \frac{A}{\Delta x_1 \Delta x_2} = \left| \frac{\partial f_1 \partial f_2}{\partial x_1 \partial x_2} - \frac{\partial f_1 \partial f_2}{\partial x_2 \partial x_1} \right| . \]  

(5.9)
The advantage of this representation is that \( A_N \) represents a measure of the sensitivity which is independent of the intervals between the lines of constant unknowns, \( \Delta x_1 \) and \( \Delta x_2 \). With this definition of the normalized area, the best sensitivity may be obtained by minimizing the function

\[
F = \frac{1}{A_N^2}.
\]

(5.10)

Thus, by minimizing \( F \), the sensitivity, \( A_N \), is maximized.

It should be noted that the normalized grid area, \( A_N \) (given by equation (5.9)), is equal to the Jacobian [82] of the system of non-linear equations

\[
f_1(x_1, x_2) - f_{1,\text{exp}} = 0
\]

\[
f_2(x_1, x_2) - f_{2,\text{exp}} = 0,
\]

(5.11)

where the subscript \( \text{exp} \) refers to the experimentally measured value. The Jacobian is defined as the determinant of the matrix, \([\Phi]\), where

\[
[\Phi] = \begin{bmatrix}
\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\
\frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2}
\end{bmatrix} = \begin{bmatrix}
\frac{\partial f_i}{\partial x_j}
\end{bmatrix}.
\]

(5.12)

This matrix formulation comes about when the system of non-linear equations given by equation (5.11) is linearized using a first order Taylor expansion and solving the linearized versions of the equations. This is the basis of the Newton-Raphson iterative technique of solving a system of non-linear equations. The linearized version of the system of equations is given as [82]

\[
[\Phi] \bar{\mathbf{z}} = -\bar{f},
\]

(5.13)
where the vectors \( \vec{x} \) and \( \vec{f} \) are given as \( \vec{x} = \{x_1, x_2\} \) and \( \vec{f} = \{f_1, f_2\} \). Therefore, it is seen that maximizing the sensitivity is equivalent to maximizing the Jacobian of the system of equations given by equation (5.11). If the determinant of \( [\Phi] \) is small compared to the norm of \( [\Phi] \), the system of equations (5.13) is said to be *ill-conditioned* [83]. Another method of evaluating the condition of a system of equations is called the condition number of a matrix [82]. This method will not be discussed since it is beyond the scope of the present work.

Now that the sensitivity, or equivalently, the normalized grid area, is quantitatively defined by equation (5.9), the optimum conditions can be found by minimizing the function given in equation (5.10). The optimum conditions are defined as the angle of incidence, \( \theta \), and the analyzer azimuth, \( A \), that maximize the grid area, \( A_N \). These optimum conditions depend upon the optical properties of the sample being studied or, in other words, depend upon the refractive index, \( n \) and \( k \). The optimum angle of incidence (\( \theta \)) and optimum analyzer azimuth (\( A \)) are shown in Figure 5.4 plotted as functions of the refractive index. The results shown in this figure are exactly the results found by Aspnes [52] for an ideal detector system. Under ideal detector conditions, Aspnes found that the optimum angle of incidence is equal to the principal angle,

\[
\theta_{opt} = \theta_{PA} ,
\]

(5.14)

and that the optimum analyzer azimuth is given by

\[
A_{opt} = \tan^{-1}(\rho) ,
\]

(5.15)
Figure 5.4: Optimum angle of incidence ($\theta$) and analyzer azimuth ($A$) plotted versus refractive index.
where \( p \) is the first ellipsometric parameter of the sample. The principal angle, as discussed in Section 2.4, is defined as the angle of incidence where the phase change on reflection, \( \Delta \), is equal to \( \pi/2 \). Aspnes also states that for cases of non-ideal detectors, where the signal-to-noise ratio becomes important, these optimum conditions may change.

Many ellipsometer systems are designed such that the angle of incidence is fixed. In this case, the fixed angle of incidence may not correspond to the optimum angle of incidence. For this given angle of incidence, \( \theta \), the optimum analyzer azimuth will no longer be given by equation (5.15), but will take on some new value. The optimum analyzer azimuth for a fixed angle of incidence is also evaluated by minimizing the function given in equation (5.10), except that only the analyzer azimuth, \( A \), is treated as an independent variable. Since the experimental system utilized for this study has the angle of incidence fixed at 45 degrees, the optimum analyzer azimuth for this angle of incidence was evaluated, with the results shown in Figure 5.5. Comparing Figures 5.4–5.5, it is seen that the optimum analyzer azimuth at a fixed angle of incidence of 45 degrees (Figure 5.5) is significantly different from the optimum analyzer azimuth found when the angle of incidence is also allowed to take on its optimum value.

For example, a material with refractive index \( n = 2 \) and \( k = 1 \) would have an optimum analyzer azimuth of approximately 36 degrees when the angle of incidence is fixed at 45 degrees, but would have an optimum analyzer azimuth
Figure 5.5: Optimum analyzer azimuth ($A$) for $\theta = 45^\circ$ plotted versus refractive index.
of approximately 15 degrees if the angle of incidence is allowed to take on its optimum value of approximately 71 degrees.

The sensitivity is plotted as functions of the refractive index in Figures 5.6–5.7 for a fixed angle of incidence and a fixed analyzer azimuth. Comparing Figures 5.6 and 5.7, it is seen that the conditions \( \theta = 70^\circ \) and \( A = 15^\circ \) (Figure 5.6) yields, in general, much higher sensitivities than the conditions \( \theta = 45^\circ \) and \( A = 35^\circ \) (Figure 5.7). It is also seen in these figures that the sensitivity approaches zero as the imaginary part of the refractive index, \( k \), approaches zero for a fixed angle of incidence and a fixed analyzer azimuth. The sensitivity does not approach zero as \( k \) approaches zero if the angle of incidence, \( \theta \), and the analyzer azimuth, \( A \), are allowed to take on their optimum values. Instead, the sensitivity approaches infinity as \( k \) approaches zero under these conditions. As noted previously, the optimum angle of incidence is given as the principal angle, which becomes identically equal to the Brewster angle at \( k = 0 \). At the Brewster angle, the parallel component of reflectivity, \( R_{||} \), becomes zero and therefore, the first ellipsometric parameter, \( \rho \), becomes zero as \( k \) approaches zero. Therefore, the optimum analyzer azimuth, \( A \), is given as zero by equation (5.15). As \( \rho \) and \( A \) simultaneously approach zero, the intensity reaching the detector becomes zero (see equation (3.10)). The fact that sensitivity increases to infinity as \( k \) approaches zero (at optimum conditions) is a result of assuming ideal detector. As the intensity reaching the detector approaches zero, the signal-to-noise ratio
Figure 5.6: Sensitivity versus refractive index for a fixed angle of incidence, $\theta = 70^\circ$, and a fixed analyzer azimuth, $A = 15^\circ$. 
Figure 5.7: Sensitivity versus refractive index for a fixed angle of incidence, $\theta = 45^\circ$, and a fixed analyzer azimuth, $A = 35^\circ$. 
of an actual, non-ideal detector will become important. If signal-to-noise ratio is considered, the conditions given by equations (5.14)-(5.15) may no longer be optimum [52].

5.3 The Effects of Polarizer Leakage

Up to this point, the polarizer and analyzer have been considered to be ideal linear polarizing elements, with their Mueller matrices being given by equations (2.34)-(2.35). An ideal linear polarizer can be described as a device which transmits no light when the incident light is linearly polarized perpendicular to that azimuth. In the practical sense, no real polarizer completely extinguishes this component of radiation polarized perpendicular to the transmission axis. The effectiveness of a real polarizer is characterized by the extinction ratio, which is defined as [39,84]

$$e = \frac{k_2}{k_1} = \frac{\tau_{\text{min}}}{\tau_{\text{max}}}$$

where $k_1$ and $k_2$ are the first and second principal transmittances of the polarizer, respectively. The quantities $\tau_{\text{min}}$ and $\tau_{\text{max}}$ refer to the minimum and maximum transmittances of linearly polarized beam of light through the polarizer as it is rotated azimuthally. An ideal polarizer has an extinction ratio of zero. It can be shown with the aid of Mueller calculus that the transmittance ($\tau$) of a linearly polarized beam through a polarizer is given as

$$\tau = k_1 \cos^2(\alpha) + k_2 \sin^2(\alpha)$$
where $\alpha$ is the azimuthal angle between the transmission axis of the polarizer and the plane of polarization of the incident beam. Equation (5.17) is known as the Law of Malus [41].

Since all real polarizers exhibit some leakage, it is useful to derive the Mueller matrix of a real polarizer. A real linear polarizer may be thought of as a partial linear polarizer. Although a partial linear polarizer may exhibit some birefringence [41,85], it will be assumed in this study that the polarizers are not birefringent (i.e. have zero retardation). The Mueller matrix of a partial linear polarizer positioned at the zero azimuth is given as [33,41]

$$
\begin{bmatrix}
(\tau_{\text{max}} + \tau_{\text{min}}) & (\tau_{\text{max}} - \tau_{\text{min}}) & 0 & 0 \\
(\tau_{\text{max}} - \tau_{\text{min}}) & (\tau_{\text{max}} + \tau_{\text{min}}) & 0 & 0 \\
0 & 0 & 2\sqrt{\tau_{\text{max}}\tau_{\text{min}}} & 0 \\
0 & 0 & 0 & 2\sqrt{\tau_{\text{max}}\tau_{\text{min}}}
\end{bmatrix}.
$$

(5.18)

Using the definition of the extinction ratio (equation (5.16)), $[\tilde{P}_0]$ may be written as

$$
[\tilde{P}_0] = \frac{\tau_{\text{max}}}{2} \begin{bmatrix}
(1 + e) & (1 - e) & 0 & 0 \\
(1 - e) & (1 + e) & 0 & 0 \\
0 & 0 & 2\sqrt{e} & 0 \\
0 & 0 & 0 & 2\sqrt{e}
\end{bmatrix}.
$$

(5.19)

Although this is a complete description of a partial linear, non-birefringent polarizer at the zero azimuth, for practical purposes it is necessary to be able to describe the polarizer at any azimuthal position. This can be done using the law
of transformation of the Mueller matrix (equation (2.33)), which yields

\[ [\tilde{P}] = [R(-\alpha)][\tilde{P}_0][R(\alpha)] \]

\[ = \frac{T_{\text{max}}}{2} (1 + e) \begin{bmatrix} 1 & Rc & Rs & 0 \\ Rc & c^2 + Qs^2 & sc(1-Q) & 0 \\ Rs & sc(1-Q) & s^2 + Qc^2 & 0 \\ 0 & 0 & 0 & Q \end{bmatrix}, \] (5.20)

where

\[ R = \frac{1 - e}{1 + e}, \] (5.21)

\[ Q = \frac{2\sqrt{e}}{1 + e}, \] (5.22)

\[ s = \sin(2\alpha) \] (5.23)

and

\[ c = \cos(2\alpha). \] (5.24)

With this definition of a partial linear polarizer, the Mueller matrix of a PSA ellipsometer may be expressed as

\[ [M] = [\tilde{A}][S][\tilde{P}], \] (5.25)

where \([S]\) represents reflection from a surface and \([\tilde{P}]\) and \([\tilde{A}]\) designate a partial linear polarizer and analyzer, respectively. Equation (5.25) is analogous to equation (3.1), where the matrices representing ideal polarizing elements ([\(P\)] and [\(A\)]) have been replaced by the matrices representing partial linear polarizers ([\(\tilde{P}\)] and [\(\tilde{A}\)]). The intensity of unpolarized light transmitted through a PSA ellipsometer is given by the [1,1] element of the \([M]\) matrix in equation (5.25). Therefore, this
equation can be used to predict the error in calculating the refractive index when using non-ideal polarizers. Using the intensity predicted by equation (5.25), the Fourier coefficients are computed as usual (equations (3.4)-(3.8)) and then the ellipsometric parameters of the sample are calculated (equations (3.17)-(3.18)). The refractive index found from these ellipsometric parameters, using equations (2.50)-(2.53), are then compared to the refractive index originally assumed when generating the $[5]$ matrix in equation (5.25). Figure 5.8 shows the deviation of the refractive index of a carbonaceous sample ($n = 2.5 - 1.0i$) as a function of the polarizer extinction ratio. The polarizer and analyzer are assumed to have the same extinction ratio (identical properties). The dotted lines in Figure 5.8 show the values of $n$ and $k$ that would be inferred from experimental measurements taken at an angle of incidence of 45 degrees with polarizing elements having a given extinction ratio. Figure 5.9 depicts the same information as Figure 5.8, except the that angle of incidence is 70 degrees. Clearly, when measurements are performed at an angle of incidence of 70 degrees, the effect of poor polarizer quality (large extinction ratio) is much less pronounced as compared with effects at an angle of incidence of 45 degrees. This is to be expected from the discussions in Section 5.1 and 5.2 concerning sensitivity versus angle of incidence. It also to be expected (from an analysis of Figures 5.1-5.2) that the problems caused by poor polarizer quality are more exaggerated as the refractive index increases. This is seen to be true in Figures 5.10-5.11, where the sample refractive index is
Figure 5.8: Deviation of the inferred refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) of $\bar{n} = 2.5 - 1.0i$ at an angle of incidence $\theta = 45^\circ$ and an analyzer azimuth $A = 35^\circ$. 
Figure 5.9: Deviation of the inferred refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) of $\tilde{n} = 2.5 - 1.0i$ at an angle of incidence $\theta = 70^\circ$ and an analyzer azimuth $A = 35^\circ$. 
chosen to $\tilde{n} = 4.5 - 2.0i$, which is a representative value for carbon in the near infrared wavelengths. Once again it is seen that the effects of polarizer leakage are more pronounced at an angle of 45 degrees as compared to 70 degrees.

Since in many practical applications, spectral measurements are required, it is instructive to assess the sensitivity of the ellipsometry technique in terms of the spectral characteristics of the polarizers. Three different polarizers (available in this laboratory) that cover the spectral range 0.35\(\mu m\) to 4.0\(\mu m\) were utilized. The polarizers used are shown in Table 5.1. The extinction ratios of these polarizers are shown in Figure 5.12, where it can be seen that the extinction ratio depends very heavily on wavelength. It follows from Figures 5.8–5.11 that with

<table>
<thead>
<tr>
<th>Polarizer</th>
<th>Spectral Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-Visible Film</td>
<td>0.35–0.75(\mu m)</td>
</tr>
<tr>
<td>Oriel #27340</td>
<td></td>
</tr>
<tr>
<td>Near IR Film</td>
<td>0.75–2.0(\mu m)</td>
</tr>
<tr>
<td>Oriel #27360</td>
<td></td>
</tr>
<tr>
<td>Gold Wire Grid</td>
<td>2.0–35(\mu m)</td>
</tr>
<tr>
<td>Perkin Elmer #186-040</td>
<td></td>
</tr>
</tbody>
</table>

the available polarizers (Figure 5.12), only certain portions of the spectrum will yield results with reasonable accuracy. If the refractive index of carbon is assumed to vary linearly on a semi-logarithmic scale, as shown by the solid lines in
Figure 5.10: Deviation of the inferred refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) of $\hat{m} = 4.5 - 2.0i$ at an angle of incidence $\theta = 45^\circ$ and an analyzer azimuth $A = 35^\circ$. 
Figure 5.11: Deviation of the inferred refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) of $\tilde{m} = 4.5 - 2.0i$ at an angle of incidence $\theta = 70^\circ$ and an analyzer azimuth $A = 35^\circ$. 
Figure 5.12: Spectral dependence of the extinction ratios of the available polarizers.
Figures 5.13–5.14 (2.5 < n < 4.5, 1 < k < 2), we can use the preceding analysis technique to determine the deviation of the refractive index due to polarizer imperfection. In Figure 5.13, we see the spectral deviation of the refractive index (dotted lines) from the theoretical value (solid lines) when an angle of incidence of 45° is utilized. The same information is shown in Figure 5.14, where an angle of incidence of 70° was utilized. Once again, it can be seen that the errors caused by imperfect polarizers is greatly magnified at θ = 45° as compared to θ = 70°. At an angle of incidence of 45°, only the spectral ranges 0.4–0.7μm and 1.3–1.6μm yield reasonably accurate results. These results emphasize the importance of choosing large angles of incidence (approximately 70°).

It should be noted that the present sensitivity analysis could not be used to correct the results for the non-ideal behavior of the polarizers. Such a correction requires accurate knowledge of the $[L]$ and $[D]$ matrices mentioned in Chapter 3. Furthermore, the degree of birefringence of the polarizers must be known spectrally.

5.4 Summary

This chapter has emphasized the importance of the choice of incidence angle and polarizer quality when performing ellipsometric measurements. The optimum angle of incidence depends upon the properties of the sample and is therefore different for different materials or for the same material at different wavelengths.
Figure 5.13: Deviation of the measured refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) at an angle of incidence ($\theta$) of 45° and an analyzer azimuth ($A$) of 35°. The polarizing elements have the extinction ratios shown in Figure 5.12. The theoretical values of the complex refractive index are $2.5 < n < 4.5$ and $1 < k < 2$. 
Figure 5.14: Deviation of the measured refractive index (dotted lines) due to polarizer leakage from its theoretical value (solid lines) at an angle of incidence ($\theta$) of 70° and an analyzer azimuth ($A$) of 35°. The polarizing elements have the extinction ratios shown in Figure 5.12. The theoretical values of the complex refractive index are $2.5 < n < 4.5$ and $1 < k < 2$. 
In general, the optimum angle of incidence is in the vicinity of the principle angle and thus the Brewster angle. Therefore, an angle of incidence of 70° is a good choice for an ellipsometer system which may be used to measure the refractive index of a variety of materials. The choice of a higher angle of incidence would also yield a better signal-to-noise ratio because of the higher reflectivity of the sample and also because of the lower thermal emission from the sample in high temperature environments. This chapter has also emphasized the need for high quality polarizers (small extinction ratios) when interpreting ellipsometric data.
Chapter 6
Experimental Considerations

Because a significant portion of the present study is experimental, a presentation of the pertinent experimental aspects of this study is necessary. The areas to be discussed in this chapter include the experimental apparatus, experimental limitations, sample preparation, and an error analysis.

6.1 Experimental Apparatus

The experimental apparatus, shown by the schematic in Figure 6.1, is comprised of an optical system centered around a high temperature chamber. The function of the high temperature chamber is to provide a temperature controlled inert environment from which optical measurements are possible. The optical system utilized is in the configuration of a PSA ellipsometer, which is characterized by a sample (S) located between a polarizer (P) and an analyzer (A).
Figure 6.1: Schematic of PSA ellipsometer centered around a high temperature furnace. LS is the Xenon arc light source, C1 and C2 are curved first surface mirrors (200 mm focal length), P1 and P2 are plane first surface mirrors, W1 and W2 are quartz cell windows of the furnace, P and A are the polarizer and analyzer, M is the monochromator, D is the detector, S is the sample, I is the iris diaphragm, F is the cut-on filter, and LC is the light chopper.
6.1.1 Optical Equipment

The optical equipment consists of three basic parts: (i) the light source, (ii) the detector and (iii) the amplification unit. The light source is a 150 watt xenon arc lamp mounted in an air cooled monochromator illuminator housing, Oriel model 68700. The light is focused to a point located 63.5 mm in front of the illuminator housing by a rotary concave mirror located in the illuminator housing. A set of iris diaphragms is mounted after the exit port to provide control of the beam width. The beam is directed and focused onto the sample (S) by the plane (P1) and concave (C1) first surface mirrors. The light reflected from the sample is directed and focused onto the detector system by the plane (P2) and concave (C2) first surface mirrors. The concave mirrors (C1 and C2) have a focal length of 200 mm and all the mirrors (P1, C1, P2 and C2) are two inches in diameter. A two inch diameter dichroic sheet polarizer (Oriel model 27340) is located at the entrance (P) and exit (A) of the high temperature chamber. These polarizing elements have extinction ratios less than $10^{-3}$ for the spectral range 400–700 nm.

The first element of the detector system is the grating monochromator, Oriel model 77250. A holographic grating was utilized which covers the spectral range 180–700 nm. Other gratings are available for longer wavelength spectral regions. The monochromator is equipped with both entrance and exit slits to control the field of view of the detector and the spectral bandwidth of the radiation reaching the detector. The higher harmonics which are present when
utilizing a grating monochromator are eliminated by a cut-on wavelength filter (Oriel model 51272), which has a cut-on wavelength of 400 nm. The intensity of the radiation exiting the monochromator is measured with a photomultiplier tube, RCA model 1P28A. This photomultiplier tube has a useful spectral range of 185–700 nm.

The light beam is modulated at a frequency of 500 Hz by a light chopper (EG&G model 196) located in the beam path just after the light source. The output signal from the light chopper serves as a reference input to the lock-in amplifier that filters out the unwanted component (noise and background radiation) of the signal. The detected signal from the photomultiplier tube is amplified by a current preamplifier (EG&G model 5002) and is filtered by a lock-in amplifier (EG&G model 5207). The signal is then sent to a personal computer via an RS232 interface. The optical components utilized are summarized in Table 6.1.

6.1.2 High Temperature Unit

The high temperature unit consists of a sealed chamber, temperature controller, and power source. These three components are designed to allow the sample temperature to be monitored and controlled from 50°C to 2300°C. Heat is supplied to the sample by tungsten resistance heating elements.

The sealed chamber, shown in Figure 6.2, is a rectangular, double-walled shell measuring approximately 20 × 20 × 30 centimeters. Water flows between
Table 6.1: Optical components.

<table>
<thead>
<tr>
<th>Optical Component</th>
<th>Manufacturer/Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>polarizer</td>
<td>Oriel/27340</td>
</tr>
<tr>
<td>light source housing</td>
<td>Oriel/68700</td>
</tr>
<tr>
<td>Xe arc lamp</td>
<td>Oriel/6253</td>
</tr>
<tr>
<td>plane mirror</td>
<td>Oriel/44170</td>
</tr>
<tr>
<td>concave mirror</td>
<td>Oriel/44430</td>
</tr>
<tr>
<td>monochromator housing</td>
<td>Oriel/77250</td>
</tr>
<tr>
<td>monochromator grating</td>
<td>Oriel/77296</td>
</tr>
<tr>
<td>cut-on filter</td>
<td>Oriel/51272</td>
</tr>
<tr>
<td>light chopper</td>
<td>EG&amp;G/196</td>
</tr>
<tr>
<td>pre-amplifier</td>
<td>EG&amp;G/5002</td>
</tr>
<tr>
<td>lock-in amplifier</td>
<td>EG&amp;G/5207</td>
</tr>
<tr>
<td>photomultiplier tube</td>
<td>RCA/1P28A</td>
</tr>
</tbody>
</table>

the double walls to keep the outer surface of the shell below 150°F (66°C). The hot zone of the furnace is cylindrical in shape with a radius of two inches and a height of five inches. The hot zone is separated from the outer chamber walls by seven layers of tungsten and molybdenum thermal radiation shields. Two tungsten mesh heating elements are located inside the hot zone to provide heat to the sample. The high temperature chamber is designed such that it can be operated under vacuum conditions or under an inert gas environment. The vacuum is supplied by a Stokes mechanical vacuum pump attached to the shell housing. The minimum pressure attainable with this unit is 10–50 millitorr, depending on the cleanliness of the chamber. If an inert gas is desired, the operating pressure is 2 psig (14 kPa), which is maintained by continuous flow of inert gas into
the chamber at a rate of 1–2 cubic feet per hour (0.47–0.94 liters/min). The inert gas escapes through a small relief valve which is activated at a pressure greater than or equal to 2 psig (14 kPa). The sample holder is a circular, flat base 1 inch (2.54 cm) in diameter, supported on the end of a cylindrical rod 5 inches (13 cm) long and 0.5 inches (1.3 cm) in diameter. The entire assembly is made of fiber-reinforced graphite and was machined by Beaumac, Inc. (Epsom, New Hampshire). This graphite rod is attached to a precision adjustable linear feed-through (MDC, model K150-MLM-2) located on the bottom of the furnace chamber. The mechanism provides adjustment for the vertical position of the sample over a two inch (5.1 cm) range of motion. The graphite rod of the sample holder gains access to the hot zone through a small circular opening (approximately 1.5 cm in diameter) in the bottom of the thermal radiation shields. Optical access into the furnace chamber for ellipsometry measurements is provided by fused silica windows, designated as W1 and W2 in Figure 6.1, and optical access into the hot zone is provided by rectangular slits (0.6 x 2.5 cm) in the radiation shields. The sealed furnace chamber is manufactured by Centorr Furnaces, Inc. (Suncook, New Hampshire).

The temperature controller is a PID controller manufactured by Barber-Colman, Inc. (Loves Park, Illinois). The controller accepts feedback from either a thermocouple or an optical pyrometer. The thermocouple can be used from room temperature up to a maximum temperature of 2000°C. At temperatures above
Figure 6.2: High temperature furnace chamber.
2000°C, the thermocouple must be retracted from the hot zone to avoid damage, and the optical pyrometer is utilized to monitor the furnace temperature. The optical pyrometer is a device which measures temperature by optically sensing the radiation emitted from a body, and this particular model can be utilized in the temperature range 1100°C–2300°C. For this study, the maximum temperature utilized was less than 2000°C and therefore, only the thermocouple was used. As seen in Figure 6.2, the retractable thermocouple interferes with the light beam when it is placed in the center of the hot zone. Therefore, it must be positioned at the edge of the hot zone during ellipsometry measurements. Since the edge of the hot zone is cooler than the center, the centerline temperature of the hot zone must be correlated with the temperature sensed at the edge of the hot zone. This correlation was performed by allowing the temperature of the furnace to reach equilibrium at a given temperature, and then measuring the temperature at both the center and the edge of the hot zone. This procedure was carried out under the three inert gases nitrogen, argon and helium. The results are shown in Table 6.2.

The power source for the high temperature furnace consists of a step-down transformer matched to the heat zone load and a silicon controlled rectifier (SCR) for continuously modulating power input to the furnace. The step-down transformer operates at 480 volt, single phase input and delivers 16 volt, single phase output. Power is delivered to the tungsten heating elements by a set of
Table 6.2: Centerline temperature of the hot zone correlated with the edge temperature.

<table>
<thead>
<tr>
<th>$T_{center}(°C)$</th>
<th>Nitrogen $T_{edge}(°C)$</th>
<th>Argon $T_{edge}(°C)$</th>
<th>Helium $T_{edge}(°C)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>21</td>
<td>21</td>
<td>21</td>
</tr>
<tr>
<td>200</td>
<td>145</td>
<td>130</td>
<td>155</td>
</tr>
<tr>
<td>400</td>
<td>270</td>
<td>250</td>
<td>310</td>
</tr>
<tr>
<td>600</td>
<td>430</td>
<td>405</td>
<td>480</td>
</tr>
<tr>
<td>800</td>
<td>620</td>
<td>610</td>
<td>670</td>
</tr>
<tr>
<td>1000</td>
<td>—</td>
<td>830</td>
<td>885</td>
</tr>
<tr>
<td>1200</td>
<td>—</td>
<td>1065</td>
<td>1120</td>
</tr>
</tbody>
</table>

water-cooled cables. These cables attach to feed-throughs on the outside of the chamber and the feed-throughs supply current into the chamber to the tungsten resistance heating elements.

### 6.2 Sample Preparation

As stated earlier, three different carbonaceous samples were utilized for this study: (i) amorphous carbon, (ii) pyrolytic graphite and (iii) a compressed soot pellet. The amorphous carbon utilized for this study is tradenamed POCO Graphite and the grade is designated DFP-1. This material is isotropic and homogeneous and may have impurities in concentrations as high as 700 parts per million. The amorphous carbon was supplied in the form of a plate which measured $4 \times 6 \times 0.25$ inches ($10 \times 15 \times 0.6$ cm). A sample measuring $1 \times 1 \times 0.25$ inches
(2.5 x 2.5 x 0.6 cm) was cut from this plate. The pyrolytic sample utilized for this study is supplied by Phizor Chemical Corporation (Easton, Pennsylvania). This sample is disc-shaped, with a radius of one inch (2.54 cm) and a thickness of 0.25 inches (0.6 cm). Pyrolytic graphite has properties very similar to those of a natural graphite crystal. In fact, it has been found [64] that the refractive indices of pyrolytic graphite are very much like that of a natural graphite crystal. Pyrolytic graphite is highly anisotropic and possesses a definite crystal structure. This crystal structure is in the form of hexagonal platelets stacked on top of each other. The pyrolytic sample has impurities totaling less than 15 parts per million.

Although it was shown in Chapter 4 that ellipsometry measurements can be performed on samples with moderately rough surfaces, it was also stated that a large roughness decreases the amount of radiation reflected into the detector. Therefore, a smooth surface will provide higher signal-to-noise ratios and more repeatable results. The amorphous carbon and pyrolytic graphite surfaces were made smooth by polishing them on successively finer silicon carbide emery papers, with grit sizes ranging from 600 to 4000.

The preparation of the compressed soot sample is more difficult than that of the other carbonaceous samples. The procedure utilized to prepare the compressed soot pellet was adopted from the work of references [5] and [86]. The soot was first collected from a premixed propane-oxygen flame over a flat flame
burner. The flat flame burner consists of a porous plug through which premixed fuel and oxygen flow. The porous plug is water cooled to prevent overheating. Nitrogen flows through an annular ring around the porous plug. This nitrogen shroud stabilizes the flame and prevents air entrainment into the flame. The soot is collected from the flame by allowing the soot to deposit on a stabilizing ceramic honeycomb, which is placed 30 cm above the burner surface. After a sufficient amount of soot is deposited on the honeycomb (after approximately 15 minutes), the honeycomb is allowed to cool and the soot is scraped from the honeycomb surface. The soot is then dried in a vacuum oven at a temperature approximately 100°C over a 12 hour period. The soot is then crushed into a fine powder and compressed in a stainless-steel piston cylinder arrangement. The soot is slowly compressed to a maximum pressure of 40,000 psi (275 MPa) in a hydraulic press. The face of the piston is polished to a very fine surface finish so that the face of the soot pellet will also be very smooth. This soot pellet is left in the stainless-steel cylinder to perform ellipsometry measurements. It should be noted that the soot pellet cannot be removed from the cylinder because of the brittle nature of the soot.

6.3 Experimental Limitations

The accuracy and precision of the ellipsometry technique described in this report may be affected by either imperfections in the experimental apparatus or by shortcomings in the mathematical model used to describe the system. Factors
that may affect accuracy are polarizer leakage, polarizer wobble, and error in
determining the angle of incidence, \( \theta \). The precision of the results is influenced
by detector noise, where the detector noise depends upon the nature of the
detector device and the signal-to-noise ratio [52,87]. A sensitivity analysis of the
ellipsometry technique has been presented in Chapter 5 and the effects of angle
of incidence and polarizer leakage were discussed. This section will present (i) a
brief discussion on the factors that affect signal-to-noise ratio, (ii) the effects of
polarizer wobble and (iii) the difficulties encountered when the optical properties
of dielectric samples are to be measured.

6.3.1 Signal-to-Noise Ratio

Several factors may affect the signal-to-noise ratio of the ellipsometry measure­
ment technique. The signal refers to intensity which leaves the source and reaches
the detector by reflection from the sample. The magnitude of the signal is in­
fluenced by the power of the source lamp and the reflectivity of the sample.
Therefore, a rough sample which diffuses the reflected radiation will decrease the
signal-to-noise ratio. The noise in the signal may consists of several components,
but can be divided into two categories: (i) noise in the light signal and (ii) noise
in the detector. Noise in the light signal originates from background sources
such room lights and sample emission due to thermal radiation. Sample emis­
ion is negligible for room temperature measurements but can become significant
for high temperature studies such as the present. Random fluctuations in the
source intensity are also considered as noise. Noise in the photomultiplier tube is caused by the electrical noise associated with the anode dark current [88]. In spectral regions where the radiant sensitivity of the photomultiplier tube is low, the signal reaching the anode will decrease, and therefore the signal-to-noise ratio will deteriorate. This study is concerned with the properties of carbonaceous materials in the wavelength range 400–700 nm and a UV-visible photomultiplier tube (RCA model 1P28A) was used as the detector. This tube has a useful spectral range of 185–700 nm, but the radiant sensitivity of this tube is very low in the wavelength range 640–700 nm. Therefore, the accuracy and repeatability of the experimental measurements are poorer in this spectral region than in the wavelength range 400–635 nm.

6.3.2 Polarizer Wobble

Polarizers are inserted in the beam path to effect a change in beam polarization, but these elements should not displace or change the direction of the beam. If the plane of the polarizer is not exactly perpendicular to the beam, the beam will be displaced in much the same way that a beam is displaced when traveling through a sheet of plate glass at non-normal incidence. As the polarizer is rotated, the beam displacement will change direction ("wobble") if the rotation axis is not parallel to the normal of the polarizer face. This beam wobble causes a different portion of the source (which usually has a different radiant intensity) to be imaged onto the detector. The amount of beam wobble depends upon the
optical pathlength of the polarizer (i.e. sheet thickness) and the amount the polarizer rotation axis may deviate ("wobble") from its ideal position.

The effect of this changing beam displacement is to cause the intensity versus polarizer azimuth curve to vary from its expected functional form of a three term \((a_0, a_2, b_2)\) Fourier series. The effects of beam wobble can be reduced by measuring the intensity over the full 360° of the polarizer azimuth, even though the period of the intensity function is only 180°. For an ideal system, measurements at only three polarizer azimuths are sufficient to calculate the three Fourier coefficients, but for a real ellipsometer system, experimental uncertainty is reduced by measuring the intensity at 20° intervals of the polarizer azimuth over a full polarizer revolution. In the course of this study, it was found that the refractive index could be in error by more than 20% (compared to a BK-7 calibration sample) when only three experimental measurements are utilized to calculate the Fourier coefficients. On the other hand, the error in refractive index is reduced to less than five percent when the intensity is measured at 20° intervals.

As stated previously, beam wobble will cause a different portion of the source, which usually has a different radiant intensity, to be imaged onto the detector. The effect of this on ellipsometry measurements is minimized by recording intensity measurements over an entire revolution of the polarizer, which tends to average the deviations caused by polarizer wobble. Another method of dealing
with the effects of polarizer wobble is to insert a diffuser in the beam path just ahead of the monochromator entrance slit. The diffuser will decrease the intensity on the detector somewhat but will minimize the effects of small beam misalignments. Therefore, a diffuser is even useful on a system where polarizer wobble is not a problem. A diffuser was not available for this study, but it was found that measuring the intensity over a full rotation of the polarizer gives satisfactory results.

6.3.3 Dielectric Samples

As may be seen from equations (3.13)–(3.18), the measured Fourier coefficients are used to provide solutions for the ellipsometric parameters in terms of \( \rho \) and \( \cos(\Delta) \). Therefore, as \( \cos(\Delta) \) approaches ±1, the error in \( \sin(\Delta) \) becomes infinitely large. As can be seen from equations (2.50)–(2.53), the imaginary part \( (k) \) of the complex refractive index is directly proportional to \( \sin(\Delta) \) for values of \( \Delta \) where \( \cos(\Delta) \) approaches ±1. Since a dielectric (transparent material; \( k = 0 \)) is characterized by \( \cos(\Delta) = \pm 1 \) at all angles of incidence, the ellipsometric technique is very poor for determining the complex refractive index of transparent or semi-transparent materials. The ellipsometric technique can be used to determine the real part \( (n) \) of the complex refractive index of these semi-transparent materials if it is assumed beforehand that \( \cos(\Delta) = \pm 1 \).

The phase, \( \Delta \), upon reflection from a bare substrate is shown versus angle of incidence for materials of various refractive indices in Figure 2.5. It is seen
that $\Delta$ is $180^\circ$ at $\theta = 0^\circ$ for all materials and becomes $0^\circ$ at $\theta = 90^\circ$ for all materials. The argument from the preceding paragraph demonstrates why the maximum precision occurs at angles of incidence in the vicinity of the principle angle, which is defined as the angle of incidence at which $\Delta = 90^\circ$. The preceding argument also explains why it may be difficult to accurately infer the complex refractive index of even moderately absorbing materials at an angle of incidence $\theta = 45^\circ$. Referring to Figure 2.5, it is seen that the phase is still close to $180^\circ$ at $\theta = 45^\circ$ for most materials, resulting in large uncertainties for $\sin(\Delta)$, and therefore, large uncertainties in the complex refractive index.

The insertion of a compensator (waveplate) of retardation ($\delta$) in the beam path just after the polarizer will improve the sensitivity of the ellipsometry technique as it is applied to dielectric materials [52]. This is because the system with a compensator will measure $\cos(\Delta - \delta)$ instead of $\cos(\Delta)$. In other words, a system which measures $\cos(\Delta - \delta)$ can determine $\Delta$ with maximum precision when $\cos(\Delta - \delta) = 0$, but $\Delta$ becomes indeterminant when $|\cos(\Delta - \delta)| \to 1$ [52]. Therefore, the retardation of the compensator should be 90 degrees when measurements are carried out on a dielectric sample. It should be noted that a compensator with retardation equal to 90 degrees is called a quarter-wave plate. This discussion also makes it clear that the addition of a compensator to the present experimental system could improve the sensitivity of ellipsometry measurements on conducting (non-dielectric) samples because the angle of incidence
is not near the principal angle. The retardation of the compensator (δ) should be chosen such that \(\cos(\Delta - \delta) \approx 0\). From the preceding discussion, it is seen that a compensator can greatly improve the sensitivity of the ellipsometry technique. The primary drawback of utilizing compensators in spectral measurements is that the compensator must be carefully calibrated at each wavelength of interest.

6.4 Error Analysis

In Chapter 5 the sensitivity of the ellipsometry technique was considered and the conditions which produce optimum sensitivity were found. The sensitivity was considered in only relative terms and nothing was stated about the absolute precision of the measurements. This section (§6.4) will consider the effects of errors in the measured intensities on the inferred refractive indices. The effects of errors in the angle of incidence and analyzer azimuth will also be considered.

6.4.1 Errors in Intensity Measurements

As shown in Figure 3.5, the measured intensities are used to calculate the normalized Fourier coefficients \((a_2, b_2)\), which are in turn utilized to calculate the refractive index \((n, k)\). Therefore, the error in the Fourier coefficients must first be found. As stated in Chapter 3, the Fourier coefficients are found from a set of experimental measurements as

\[
a_0 = \frac{1}{N} \sum_{k=1}^{N} I_k ,
\]  

(6.1)
\[
\tilde{a}_2 = \frac{2}{N} \sum_{k=1}^{N} I_k \cos(2P_k)
\]  
(6.2)

and

\[
\tilde{b}_2 = \frac{2}{N} \sum_{k=1}^{N} I_k \sin(2P_k)
\]  
(6.3)

where \(I_k\) is the experimental intensity readings at equally spaced azimuthal settings of the polarizer, \(P_k\), and \(N\) is the number of experimental measurements.

The standard error, \(\sigma_N\), of \(a_0\) is given as [89]

\[
\sigma_N(a_0) = \left\{ \sum_{k=1}^{N} \left[ \left( \frac{\partial a_0}{\partial I_k} \right) \sigma(I_k) \right]^2 \right\}^{1/2},
\]  
(6.4)

where \(\sigma(I_k)\) represents the standard error in the measurement of \(I_k\). If the standard error of the intensity measurements, \(\sigma(I_k)\), are constant with respect to \(k\), the standard error of \(a_0\) can be written as

\[
\sigma_N(a_0) = \sigma(I)/N^{1/2}.
\]  
(6.5)

Note that in general, the standard error of the intensity measurements is not independent of \(k\), but will vary as the intensity varies. Nevertheless, this approximation will provide valuable insight to the error analysis.

The adjusted standard error, \(S_N\), is related to the standard error as [89]

\[
S_N(a_0) = \sigma(a_0) \left[ \frac{N}{N - 3} \right]^{1/2},
\]  
(6.6)

where the 3 in the denominator signifies that at least three quantities must be measured to calculate the three Fourier coefficients in equations (6.1)–(6.3).
Therefore, the adjusted standard error of $a_0$ can be written in terms of the standard error of the intensity measurements, $\sigma(I)$, as

$$S_N(a_0) = \frac{\sigma(I)}{(N - 3)^{1/2}} ,$$  \hspace{1cm} (6.7)

where $N$ represents the number of experimental measurements. Similarly, the adjusted standard error in the other Fourier coefficients are found as

$$S_N(\tilde{a}_2) = S_N(\tilde{b}_2) = \left[ \frac{2}{N - 3} \right]^{1/2} \sigma(I) .$$  \hspace{1cm} (6.8)

Equations (6.7)–(6.8) are the adjusted standard errors in the standard (non-normalized) Fourier coefficients, but the normalized Fourier coefficients are needed to calculate the optical properties. The normalized Fourier coefficients are related to the standard Fourier coefficients as

$$a_2 = \frac{\tilde{a}_2}{a_0} ,$$  \hspace{1cm} (6.9)

and

$$b_2 = \frac{\tilde{b}_2}{a_0} .$$  \hspace{1cm} (6.10)

The adjusted standard error in the normalized Fourier coefficients is given as

$$S_N(a_2) = \left\{ \left[ \left( \frac{\partial a_2}{\partial \tilde{a}_2} \right) S_N(\tilde{a}_2) \right]^2 + \left[ \left( \frac{\partial a_2}{\partial a_0} \right) S_N(a_0) \right]^2 \right\}^{1/2} .$$  \hspace{1cm} (6.11)

Substituting equations (6.7)–(6.10) into equation (6.11) yields

$$S_N(a_2) = \frac{\sigma(I)}{(N - 3)^{1/2} a_0} \left[ 2 + a_2^2 \right]^{1/2} .$$  \hspace{1cm} (6.12)
Similarly, the adjusted standard error in $b_2$ is found as

$$S_{N}(b_2) = \frac{\sigma(I)}{(N - 3)^{1/2}} \frac{a_0}{a_0} [2 + b_2^2]^{1/2}. \quad (6.13)$$

Although equations (6.12)—(6.13) were derived with the simplifying assumption that $\sigma(I_k) = \sigma(I)$ for all $k$, these equations provide valuable information about the error analysis. The first thing to note is that since $a_2$ and $b_2$ always lie between $-1$ and $+1$, the magnitudes of these parameters do not play a large role in the determination of error. The parameters which can be adjusted to minimize the error are $\sigma(I)$, $N$ and $a_0$. The quantity $\sigma(I)$ is a measure of the accuracy of the intensity measurements and can be decreased by using more precise detectors and a higher intensity source. The term $a_0$ represents the average intensity reaching the detector and the adjusted standard error in $a_2$ and $b_2$ can be decreased by increasing $a_0$. This is also accomplished with a higher power source. As expected, increasing the number of measurements, $N$, will also decrease the adjusted standard error of the Fourier coefficients, but because the error varies as $N^{-1/2}$, this is sometimes a costly method of improving the accuracy.

The goal of this section is to find the error in the refractive index for a given error in intensity measurements. The adjusted standard error in the refractive indices $(S_N(n), S_N(k))$ is given in terms of the adjusted standard error of the Fourier coefficients $(S_N(a_2), S_N(b_2))$ as

$$S_{N}(n) = \left\{ \left[ \left( \frac{\partial n}{\partial a_2} \right) S_N(a_2) \right]^2 + \left[ \left( \frac{\partial n}{\partial b_2} \right) S_N(b_2) \right]^2 \right\}^{1/2}. \quad (6.14)$$
and

\[ S_N(k) = \left\{ \left[ \left( \frac{\partial k}{\partial a_2} \right) S_N(a_2) \right]^2 + \left[ \left( \frac{\partial k}{\partial b_2} \right) S_N(b_2) \right]^2 \right\}^{1/2} \].

Equations (6.14)-(6.15) can be utilized to provide an estimate of the error in the inferred refractive indices once the values of \( S_N(a_2) \) and \( S_N(b_2) \) are calculated from equations (6.12)-(6.13). The standard error in intensity measurements, \( \sigma(I) \), is required in equations (6.12)-(6.13). This value is estimated from the fluctuations in the lock-in amplifier readings as approximately 1.0 percent of the average intensity reading, \( a_0 \), yielding \( \sigma(I)/a_0 \approx 0.01 \). The maximum error which occurs in the Fourier coefficients (equations (6.12)-(6.13)) is found by allowing \( a_2 = b_2 = 1 \). For this particular study, the number of measurements, \( N \), is 18. Substituting these values into equations (6.12)-(6.13) yields \( S_N(a_2) = S_N(b_2) = 0.0045 \). Before substituting these values into equations (6.14)-(6.15), the derivatives shown in these equations must be evaluated. They are evaluated numerically (utilizing central differences) at a particular value of angle of incidence, analyzer azimuth and refractive index. All measurements in this study were performed at an angle of incidence of 45 degrees and an analyzer azimuth of 35 degrees. Since the derivatives in equations (6.14)-(6.15) are dependent of the values of \( n \) and \( k \), the errors predicted by these equations will be different for the three carbonaceous samples considered, which include soot, amorphous carbon and pyrolytic graphite. The complete set of inferred refractive indices for these materials will be presented in Chapter 8, but a representative
average value can be chosen for each of these materials for the purpose of error analysis. Utilizing these average values of refractive index, the error in refractive index (predicted by equations (6.12)–(6.15)) is shown for the three carbonaceous samples in Table 6.3.

Table 6.3: Error in refractive index of carbonaceous samples due to errors in the intensity measurements for $\sigma(I)/a_0 = 0.01$, $\theta = 45^\circ$ and $A = 35^\circ$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$n$</th>
<th>$k$</th>
<th>$S_N(n)$</th>
<th>$S_N(k)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot</td>
<td>1.5</td>
<td>0.4</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Amorphous Carbon</td>
<td>2.3</td>
<td>1.0</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Pyrolytic Graphite</td>
<td>2.6</td>
<td>1.4</td>
<td>0.10</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The values shown in Table 6.3 are a conservative estimate of the errors in the inferred refractive index. It will be seen in Chapter 8 that the actual deviations between measurements is less than the values shown in Table 6.3. This is due to the fact that the standard error in intensity measurements is actually less than that assumed in this section, especially at the higher signal levels.

6.4.2 Angle of Incidence and Analyzer Azimuth Errors

In addition to the accuracy of the intensity readings, the absolute error in the inferred refractive indices also depends upon the accuracy of the angle of incidence ($\theta$) and the analyzer azimuth ($A$). The errors in inferred refractive index
due to angle of incidence errors is given as

$$\Delta n_\theta = \left| \left( \frac{\partial n}{\partial \theta} \right) \Delta \theta \right|$$  \hspace{1cm} (6.16)

and

$$\Delta k_\theta = \left| \left( \frac{\partial k}{\partial \theta} \right) \Delta \theta \right|$$  \hspace{1cm} (6.17)

where $\Delta \theta$ is the error in the angle of incidence. Similarly, the error in inferred refractive index due to error in analyzer azimuth is given as

$$\Delta n_A = \left| \left( \frac{\partial n}{\partial A} \right) \Delta A \right|$$  \hspace{1cm} (6.18)

and

$$\Delta k_A = \left| \left( \frac{\partial k}{\partial A} \right) \Delta A \right|$$  \hspace{1cm} (6.19)

Once again, the errors in inferred refractive index are dependent upon the values of refractive index, angle of incidence and analyzer azimuth. Tables 6.4–6.5 summarize the errors in inferred refractive indices due to error in angle of incidence and analyzer position found from equations (6.16)–(6.19). As previously,

Table 6.4: Error in refractive index of carbonaceous samples due to error in the angle of incidence for $\theta = 45^\circ$, $A = 35^\circ$, and $\Delta \theta = 0.2^\circ$.

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
<th>k</th>
<th>$\Delta n_\theta$</th>
<th>$\Delta k_\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot</td>
<td>1.5</td>
<td>0.4</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>Amorphous Carbon</td>
<td>2.3</td>
<td>1.0</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>Pyrolytic Graphite</td>
<td>2.6</td>
<td>1.4</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Table 6.5: Error in refractive index of carbonaceous samples due to error in the analyzer azimuth for $\theta = 45^\circ$, $A = 35^\circ$, and $\Delta A = 0.2^\circ$.

<table>
<thead>
<tr>
<th>Material</th>
<th>n</th>
<th>k</th>
<th>$\Delta n_A$</th>
<th>$\Delta k_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soot</td>
<td>1.5</td>
<td>0.4</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Amorphous Carbon</td>
<td>2.3</td>
<td>1.0</td>
<td>0.008</td>
<td>0.01</td>
</tr>
<tr>
<td>Pyrolytic Graphite</td>
<td>2.6</td>
<td>1.4</td>
<td>0.009</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Representative average values have been chosen for the refractive indices of carbonaceous materials. The error in angle of incidence ($\Delta \theta$) and analyzer azimuth ($\Delta A$) is approximately 0.2 degrees, as described in Chapter 7.
Chapter 7

Alignment and Testing of the Experimental Facility

Proper alignment of the ellipsometer is crucial to the accuracy of the ellipsometric measurements. The alignment procedure includes accurate determination of both the angle of incidence and the azimuthal position of the polarizer and analyzer. This chapter describes the method used to align the ellipsometer with respect to angle of incidence (geometric alignment) and the method used to align the azimuthal positions of the analyzer and polarizer. The technique to azimuthally align the polarizer and analyzer was developed recently by Stagg and Charalamposoulos [90]. After completing the description of the alignment technique, a typical measurement on a carbonaceous sample is presented. Finally, the experimental system and procedure is tested by measuring the temperature dependence of the refractive index of a silicon wafer. This material is chosen for testing the system because its properties have been previously measured as a function of temperature [56] and thus a comparison is possible.
7.1 Geometric Alignment

The angle of incidence is fixed at approximately 45° by the orientation and position of the furnace windows. Therefore, the incident beam should strike the sample surface at an angle of incidence very close to 45°. Precise alignment of the angle of incidence at 45° is accomplished by placing a right angle, 45° prism on the sample holder, with the hypotenuse facing downward, as shown in Figure 7.1. The alignment prism is made from BK-7, which is an optical grade of glass. When the light beam strikes the face of the prism, it will be reflected back toward the position it originated from. Referring to Figure 7.1, if the reflected beam strikes mirror C1 in the same spot as the incident beam, the angle of incidence is then 45°. The angle of incidence can be adjusted by tilting mirror C1 and adjusting the vertical position of the sample holder. Both the vertical position of the sample and the tilt of mirror C1 are precisely controlled by micro-positioning devices. Because the beam has a finite width, it is not possible to determine if the reflected image lies precisely upon the incident image. Therefore, with a beam size of approximately 0.25 inches (0.6 cm), the angle of incidence can be set to 45° within ±0.2°. Once the incident beam is aligned, the detector system is aligned by simply directing the reflected beam into the monochromator entrance slit. The reflected beam is directed by changing the tilt angle of mirrors P2 and C2, which are both controlled with micro-positioning devices. As seen in Figure 7.1, the reflected beam originates from an internal reflection from the
Figure 7.1: Furnace chamber with alignment prism.
hypotenuse face of the alignment prism. Therefore, the ellipsometer system will be aligned with respect to the sample holder surface. To perform measurements on a sample, the vertical position of the sample holder must be lowered by an amount exactly equal to the sample thickness. An alternative method is to align the ellipsometer with respect to the sample by placing the alignment prism on the sample surface. This procedure is only possible if the sample surface will not be damaged by the alignment prism.

7.2 Method for Azimuthal Alignment in Fixed Angle Ellipsometry

In this section, a method is developed which allows alignment of the transmission axes of the polarizer and analyzer with respect to the plane of incidence. The plane of incidence is defined by the vector normal to the sample surface and a vector parallel to the incoming beam. This section (section 7.2) will introduce the need for azimuthal alignment, develop the necessary equations, and perform a numerical sensitivity analysis of the azimuthal alignment technique. Finally, some experimental results will be presented and the advantages of this alignment technique will be summarized.

7.2.1 Introduction

Azimuthal reference positions refer to the difference between the true azimuthal position of the transmission axes of the polarizer and analyzer and the reading
of the polarizer rotators. Determination of the azimuthal reference positions of
the polarizer and analyzer in an ellipsometer system is crucial to the accurate
determination of the ellipsometric parameters of the sample. For example, it has
been shown that a systematic error in the azimuthal position of the polarizer
and analyzer can lead to significant errors in the determination of the refractive
index of the sample [91]. Various methods have been proposed for the azimuthal
alignment of the polarizers of an ellipsometer system, but these methods are
based on the assumption that the relative position of the polarizer and analyzer
can be determined by a straight-through (no sample present) intensity measure­
ment [91–92]. For ellipsometer systems in which the angle of incidence is fixed,
the straight-through measurement is not possible. Therefore, it is necessary to
devise a different method for alignment of the polarizer and analyzer for such
systems. The objective of this study is to develop such a method.

7.2.2 Theory

It was shown in Chapter 3 that the intensity of light through the PSA ellipsometer
system shown in Figure 3.1 is given as

\[ I(P, A) = C_2 I_{PSA}(P, A) f_D(A) f_L(P) , \]  

(7.1)

where \( I_{PSA} \), given as

\[ I_{PSA}(P, A) = C_1 k_A k_P R_\perp \left[ \rho^2 \cos^2 (P) \cos^2 (A) + \sin^2 (P) \sin^2 (A) \right. \]

\[ \left. + \frac{\rho}{2} \cos (\Delta) \sin (2P) \sin (2A) \right] , \]  

(7.2)
is the intensity through an ideal PSA ellipsometer, and $C_2$ is a constant. The effects of the source and detector optics are given by the functions $f_D(A)$ and $f_L(P)$ as

$$f_D(A) = \left[ 1 + \frac{d_{1,2}}{d_{1,1}} \cos(2A) + \frac{d_{1,3}}{d_{1,1}} \sin(2A) \right]$$

(7.3)

and

$$f_L(P) = \left[ 1 + \frac{l_{2,1}}{l_{1,1}} \cos(2P) + \frac{l_{3,1}}{l_{1,1}} \sin(2P) \right].$$

(7.4)

The direction of positive azimuth is counterclockwise when looking into the oncoming beam.

In order to determine the ellipsometric parameters, $\rho$ and $\Delta$, of the sample, it is necessary to take measurements at various settings of the polarizer and analyzer. This emphasizes the need for accurate settings of the polarizer and analyzer. Accurate settings can be obtained with the use of high precision rotators once the reference position of the polarizer and analyzer are known with respect to the plane of incidence. Thus, it is desirable to develop a method by which the true position of the polarizer and analyzer with respect to the plane of incidence can be determined.

As may be seen from equation (7.1) the intensity of light reflected from a dielectric (transparent material) is exactly zero for specific positions of the polarizer and analyzer. This is a consequence of the fact that the phase of dielectrics exhibit only two discrete values: $\cos(\Delta) = -1$ for angles of incidence less than the Brewster angle and $\cos(\Delta) = +1$ for angles of incidence greater
than the Brewster angle. Therefore, the intensity of a beam reflected from a
dielectric in an ellipsometer system is extinguished under the condition

\[ \rho = \pm \tan(A) \tan(P) \]  

(7.5)

where the "+" sign corresponds to angles of incidence less than the Brewster
angle (where \( \cos(\Delta) = -1 \)) and the "-" sign corresponds to angles of incidence
greater than the Brewster angle (where \( \cos(\Delta) = +1 \)). For the ellipsometer
system utilized in this study, the angle of incidence is fixed at 45°, which is less
than the Brewster angle of any dielectric material. Therefore, only the "+" sign
in equation (7.5) will be considered. Equation (7.5) presents a simple way of
measuring \( \rho \) of a dielectric material, provided that the reference positions of the
polarizer and analyzer are known. As will be demonstrated in the remainder of
this section, equation (7.5) can also be utilized to find the reference positions of
the polarizer and analyzer.

Let us assume that the reference positions of the polarizer and analyzer
are unknown, and that high quality rotators are available to measure the change
in azimuth of \( P \) and \( A \). By treating \( \rho \) as unknown, three measurements of
polarizer and analyzer which null the beam are needed in order to unambiguously
determine \( \rho \) and the reference positions of the polarizer and analyzer. Letting
\( A_i = A_0 + \Delta A_i \) and \( P_i = P_0 + \Delta P_i \), equation (7.5) may be written as

\[ \rho = \tan(A_0 + \Delta A_i) \tan(P_0 + \Delta P_i) , \quad i = 1, 2, 3 \]  

(7.6)

where \( \rho \), \( A_0 \) and \( P_0 \) are unknown quantities and \((\Delta P_i, \Delta A_i)\) represent three sets
of polarizer-analyzer azimuth settings (from a reference point) which null the intensity. Thus, solution of the system of equations (7.6) for the three different settings of the polarizer-analyzer will yield \( \rho \), \( A_0 \) and \( P_0 \). The solution for \( \sin^2(2A_0) \) is given as

\[
\sin^2(2A_0) = \frac{4C_3^2 - 2(C_1 - C_2)(C_2 + C_4)}{4C_3^2 + (C_1 - C_2)^2} - \sin^2(2\Delta A_1) ,
\]

where

\[
C_1 = a^2 \cos^2(\Delta A_2 + \Delta A_1) + b^2 \cos^2(\Delta A_3 + \Delta A_1) - 2ab \cos(\Delta P_3 - \Delta P_2) \cos(\Delta A_2 + \Delta A_1) \cos(\Delta A_3 + \Delta A_1) ,
\]

\[
C_2 = a^2 \sin^2(\Delta A_2 + \Delta A_1) + b^2 \sin^2(\Delta A_3 + \Delta A_1) - 2ab \cos(\Delta P_3 - \Delta P_2) \sin(\Delta A_2 + \Delta A_1) \sin(\Delta A_3 + \Delta A_1) ,
\]

\[
C_3 = \frac{a^2}{2} \sin(2\Delta A_2 + 2\Delta A_1) + \frac{b^2}{2} \sin(2\Delta A_3 + 2\Delta A_1) - ab \cos(\Delta P_3 - \Delta P_2) \sin(2\Delta A_1 + \Delta A_2 + \Delta A_3) ,
\]

\[
C_4 = -\sin^2(\Delta P_3 - \Delta P_2) ,
\]

\[
a = \frac{\sin(\Delta P_2 - \Delta P_1)}{\sin(\Delta A_2 - \Delta A_1)}
\]

and

\[
b = \frac{\sin(\Delta P_3 - \Delta P_1)}{\sin(\Delta A_3 - \Delta A_1)}
\]

Since \( A_0 \) can only take positive values, the solution of the system of equations (7.6)
for $P_0$ yields

$$\sin (2P_0 + \Delta P_2 + \Delta P_1) = -a \sin (2A_0 + \Delta A_2 + \Delta A_1) . \quad (7.14)$$

Furthermore, the values for $\rho$ may be obtained from the relation

$$\rho = \tan (P_0 + \Delta P_1) \tan (A_0 + \Delta A_1) . \quad (7.15)$$

Equations (7.7)-(7.15) provide four sets of solutions for $(A_0, P_0$ and $\rho)$, but only one set will satisfy the original system of equations (7.6).

Although the refractive index $(n)$ of the sample need not be known to utilize this technique, at times the refractive index of the material may be known. For example, the refractive index of optical glasses is usually published by the manufacturer for a wide range of wavelengths. In such cases the refractive index of the dielectric sample can be calculated from the value of $\rho$ as

$$n = \sin (\theta) \left[ \left( \frac{1 + \rho}{1 - \rho} \right)^2 \tan^2 (\theta) + 1 \right]^{1/2} , \quad (7.16)$$

where $\theta$ is the angle of incidence. This equation was introduced in Section 2.4. Equation (7.16) provides a means of checking the calculated optical properties against those published by the manufacturer.

### 7.2.3 Sensitivity Analysis

Use of the previously described technique requires the difficult task of determining the position of the polarizer which will extinguish the beam for a given setting of the analyzer. An alternative, but equivalent, method would be to determine
the analyzer position which will extinguish the beam for a given polarizer setting. This study will only utilize the method in which the analyzer is fixed and the polarizer is rotated until the beam is extinguished. Therefore, the analyzer positions \((\Delta A_1, \Delta A_2, \Delta A_3)\) may be set with a high degree of accuracy (within 0.1°), but the corresponding polarizer settings \((\Delta P_1, \Delta P_2, \Delta P_3)\) which null the beam will be difficult to find precisely, and will consequently have some error associated with them. Assuming that the error in polarizer setting is \(\delta \Delta P\) for all three polarizer settings, the corresponding error in the three unknown quantities \((A_0, P_0, \rho)\) may be expressed as

\[
\delta A_0 = \delta \Delta P \sqrt{\left(\frac{\partial A_0}{\partial \Delta P_1}\right)^2 + \left(\frac{\partial A_0}{\partial \Delta P_2}\right)^2 + \left(\frac{\partial A_0}{\partial \Delta P_3}\right)^2}, \tag{7.17}
\]

\[
\delta P_0 = \delta \Delta P \sqrt{\left(\frac{\partial P_0}{\partial \Delta P_1}\right)^2 + \left(\frac{\partial P_0}{\partial \Delta P_2}\right)^2 + \left(\frac{\partial P_0}{\partial \Delta P_3}\right)^2}, \tag{7.18}
\]

and

\[
\delta \rho = \delta \Delta P \sqrt{\left(\frac{\partial \rho}{\partial \Delta P_1}\right)^2 + \left(\frac{\partial \rho}{\partial \Delta P_2}\right)^2 + \left(\frac{\partial \rho}{\partial \Delta P_3}\right)^2}, \tag{7.19}
\]

where \(\delta\) signifies the uncertainty in the measured or computed quantities. Clearly, the errors given in equations (7.17)–(7.19) depend upon the value of \(\rho\) and the selected settings of the analyzer \((\Delta A_1, \Delta A_2, \Delta A_3)\). In order to estimate the errors predicted by equations (7.17)–(7.19), it is assumed that the analyzer settings are chosen as

\[
\Delta A_1 = -\Delta A, \tag{7.20}
\]

\[
\Delta A_2 = 0, \tag{7.21}
\]
and

$$\Delta A_3 = +\Delta A,$$  \hspace{1cm} (7.22)

where \(\Delta A\) is some number chosen by the experimentalist. With these assumptions, the errors in equations (7.17)-(7.19) can be calculated as functions of \(\rho\), \(A_0\) and \(\Delta A\). Figure 7.2 shows the errors in \(\rho\), \(A_0\) and \(P_0\) plotted versus \(A_0\) for an error in polarizer setting \(\delta \Delta P\) of 0.5°. As may be seen from Figure 7.2, no choice of \(A_0\) simultaneously minimizes the error in \(\rho\), \(A_0\), and \(P_0\), but choosing \(A_0\) at approximately 15° seems to cause an acceptable error in the three unknowns. It is noted that since \(A_0\) is one of the unknowns it cannot be chosen precisely, but its position is usually known before alignment to within 5°. Figure 7.3 shows the error in the three unknowns as functions of \(\Delta A\). In this particular case it appears that choosing \(\Delta A\) between 35° and 40° is the best choice. Figure 7.4 shows the error in the three unknowns plotted versus the error in polarizer settings \(\delta \Delta P\). With the aid of this figure, one can estimate the error in the three unknowns if the error in polarizer setting is known. In Figures 7.2–7.4, the value of \(\rho\) was chosen to be 0.3, which is representative of optical glass in the visible wavelengths at an angle of incidence of 45°. Several other points need to be made with respect to the accuracy of the parameters \(P_0\) and \(A_0\). Specifically, since in this study, the first ellipsometric parameter, \(\rho\), is treated as an unknown, this technique can be applied at any angle of incidence, whether or not that angle of incidence is known. The azimuthal reference positions of the polarizer and
Figure 7.2: Error in $\rho$, $A_0$, and $P_0$ versus $A_0$ for an error in polarizer setting ($\delta \Delta P$) of 0.5°, with $\rho = 0.3$ and $\Delta A = 35°$. 
Figure 7.3: Error in $\rho$, $A_0$, and $P_0$ versus $\Delta A$ for an error in polarizer setting ($\delta \Delta P$) of $0.5^\circ$, with $\rho = 0.3$ and $A_0 = 15^\circ$. 
Figure 7.4: Error in $\rho$, $A_0$, and $P_0$ versus error in polarizer setting ($\delta \Delta P$), with $\rho = 0.3$, $A_0 = 15^\circ$, and $\Delta A = 35^\circ$. 
analyzer are independent of the angle of incidence and therefore lack of precise
knowledge of the angle of incidence will not affect the accuracy of $P_0$ and $A_0$.
It is only when the refractive index is calculated using equation (7.16) that the
accuracy in the angle of incidence, $\theta$, becomes important.

7.2.4 Experimental Results

The method for polarizer alignment presented in this section was tested by us-
ing a high temperature unit that is equipped with optical ports at 45° angle of
incidence and allows the sample to be heated up to a temperature of 2300°C
(see Figure 6.1). Reflection measurements were carried out on a sample of BK-7
glass at 0.58 μm and an angle of incidence of 45° ± 0.20°. At this wavelength, the
reported value of the refractive index in the literature is 1.517 [55]. The polarizer
and analyzer are mounted in polarizer rotators with positioning accuracy of ap-
proximately 0.1°. A reference mark is inscribed on these polarizers indicating the
direction of the transmission axis of the polarizer. This mark allows an approx-
imate pre-alignment of the polarizer and analyzer to within 5°–10°. Therefore,
one can choose the initial settings, $A_{0,S}$ and $P_{0,S}$ (the subscript $S$ refers to rotator
scale), and then compare these to the predicted values of $A_0$ and $P_0$ from the
solution of the system of equations (7.7)–(7.15). The difference between scale
rotator readings and the true positions of the polarizer and analyzer represents
the offset or error of the rotator readings. The offset of the polarizer ($\delta P$) and
The initial scale settings for $A$ and $P$ were chosen as $A_{0,s} = 15^\circ$ and $P_{0,s} = 10^\circ$. The settings for the analyzer were chosen as $\Delta A_1 = -35^\circ$, $\Delta A_2 = 0^\circ$ and $\Delta A_3 = 35^\circ$. The corresponding polarizer settings were found to be $\Delta P_1 = -54.0^\circ$, $\Delta P_2 = 35.9^\circ$ and $\Delta P_3 = 2.4^\circ$. With these six quantities, the unknown quantities were calculated from equations (7.7)-(7.15) as $\rho = 0.3135$, $A_0 = 15.9^\circ$ and $P_0 = 11.9^\circ$. Using this value of $\rho$ and $\theta = 45^\circ$, equation (7.16) yields a value of $n$ of 1.526 which differs only by 0.6% from the published value of 1.517. It should also be noted that the technique was tested on a room temperature reflectometer system developed in previous work [39] and yielded a value of 1.492 for $n$ which is approximately 1.7% lower than the published value. The polarizer and analyzer offsets were found to be $\delta P = 1.9^\circ$ and $\delta A = 0.9^\circ$, respectively. Although excellent agreement is achieved for the inferred refractive index, it is not possible to estimate the accuracy of the polarizer and analyzer positions. Because of the non-isotropic (birefringent) nature of the windows, the furnace windows should be removed before performing this alignment technique.
7.2.5 Summary

A method has been developed for the azimuthal alignment of the polarizer and analyzer in a PSA (polarizer-sample-analyzer) ellipsometer system. This method allows the determination of the reference positions of the polarizer and analyzer through the use of reflection measurements from a dielectric sample (of unknown refractive index) at a single angle of incidence. The developed technique eliminates the requirement for the intensity measurements in the straight-through mode, which may be impossible to be carried out under certain experimental conditions. This technique of azimuthal alignment is similar in practice to the technique described by Kawabata [93]. Kawabata’s technique consists of measuring two sets of Fourier coefficients at two analyzer azimuths 90° apart. These two sets of Fourier coefficients allow the determination of the ellipsometric parameters of the sample, \( \rho \) and \( \Delta \), and also the reference position of the polarizer and analyzer. It should be noted that Kawabata’s technique cannot be utilized with dielectric samples because the equations developed by him become indeterminant as \( k \) approaches zero.

7.3 Typical Measurement

As stated in Chapter 3, the optical properties of the sample can be determined by measuring the intensity through the ellipsometer system for a number of polarizer azimuths. A minimum of at least three measurements will allow the
determination of the Fourier coefficients \((a_0, a_2, \text{ and } b_2)\), which will yield the sample properties. As stated in this chapter, it is desirable to measure the intensity at more than three polarizer azimuths to reduce the effects of experimental uncertainty. Measuring the intensity at 20° intervals of the polarizer azimuth (18 points) is found to yield results repeatable within one percent, while a measurement interval of 10° (36 points) does not significantly improve these results. The results of a typical measurement on an amorphous carbon sample are shown in Table 7.1 and Figure 7.5. In Figure 7.5, the experimental values are compared to the curve fit of a two term Fourier series (equation (3.3) with \(a_4 = b_4 = 0\)). The calculated Fourier coefficients are shown in Table 7.2 along with the inferred optical properties. It is seen in Figure 7.5 that some of the experimental points deviate from the curve fit. This deviation is not random, but is a repeatable phenomenon thought to be caused by polarizer wobble.

In Table 7.1, the experimentally measured intensities are listed with the corresponding polarizer azimuth readings \((P_s)\). The analyzer azimuth \((A_s)\) reading is 35°. Note that the polarizer and analyzer azimuth readings are not the true settings, but are related to the true polarizer \((P)\) and analyzer \((A)\) settings by

\[
P = P_s + \delta P
\]

(7.25)

and

\[
A = A_s + \delta A
\]

(7.26)
Figure 7.5: Typical ellipsometry measurement on amorphous carbon.
Table 7.1: Experimental ellipsometry data from amorphous carbon sample at $\lambda = 400$ nm.

<table>
<thead>
<tr>
<th>$P_s$</th>
<th>Intensity</th>
<th>$P_s$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>489.3</td>
<td>180</td>
<td>482.5</td>
</tr>
<tr>
<td>20</td>
<td>154.6</td>
<td>200</td>
<td>149.3</td>
</tr>
<tr>
<td>40</td>
<td>45.1</td>
<td>220</td>
<td>45.9</td>
</tr>
<tr>
<td>60</td>
<td>206.6</td>
<td>240</td>
<td>216.6</td>
</tr>
<tr>
<td>80</td>
<td>567.8</td>
<td>260</td>
<td>584.6</td>
</tr>
<tr>
<td>100</td>
<td>961.7</td>
<td>280</td>
<td>971.9</td>
</tr>
<tr>
<td>120</td>
<td>1200.1</td>
<td>300</td>
<td>1194.7</td>
</tr>
<tr>
<td>140</td>
<td>1167.2</td>
<td>320</td>
<td>1166.9</td>
</tr>
<tr>
<td>160</td>
<td>888.7</td>
<td>340</td>
<td>886.8</td>
</tr>
</tbody>
</table>

where $\delta P$ and $\delta A$ refer to the difference between the true azimuthal positions and the azimuthal rotator readings. The values of $\delta P$ and $\delta A$ are found by the azimuthal alignment technique presented in Section 7.2. The effects of polarizer wobble can also be seen in Table 7.1. As stated in Chapter 3, the intensity is a periodic function with respect to the polarizer azimuth ($P$) with a period of $180^\circ$. Therefore, the intensities shown in the first column of Table 7.1 should be equal to the intensities in the second column of this table since the intensities were measured at polarizer azimuths which differ by $180^\circ$. In other words, the intensity measured at some polarizer azimuth, $I(P)$, should be exactly equal to the intensity measured $180^\circ$ from this polarizer azimuth, $I(P + 180^\circ)$. While the repeatability of these measurements is approximately 0.5%, polarizer wobble can cause $I(P)$ and $I(P + 180^\circ)$ to differ by 5% or more. The effects of polarizer
Table 7.2: Reduction of ellipsometry data from amorphous carbon sample at $\lambda = 400$ nm.

<table>
<thead>
<tr>
<th>Given Quantities</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Source Parameters</strong></td>
</tr>
<tr>
<td>$l_1 = 0.0054$</td>
</tr>
<tr>
<td>$l_2 = 0.0027$</td>
</tr>
<tr>
<td><strong>Window Birefringence Parameters</strong></td>
</tr>
<tr>
<td>$\alpha_1 = -26.1^\circ$, $\beta_1 = -9.2^\circ$, $\alpha_2 = 1.2^\circ$, $\beta_2 = -3.7^\circ$</td>
</tr>
<tr>
<td><strong>Analyzer Azimuth Setting</strong></td>
</tr>
<tr>
<td>$A_S = 35^\circ$</td>
</tr>
<tr>
<td><strong>Azimuthal Alignment Parameters</strong></td>
</tr>
<tr>
<td>$\delta A = 3.0^\circ$, $\delta P = -4.7^\circ$</td>
</tr>
<tr>
<td><strong>Angle of Incidence</strong></td>
</tr>
<tr>
<td>$\theta = 45^\circ$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Calculated Quantities</th>
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</thead>
<tbody>
<tr>
<td><strong>Fourier Coefficients</strong></td>
</tr>
<tr>
<td>$a'_2 = -0.3766$, $b'_2 = -0.8514$</td>
</tr>
<tr>
<td><strong>Ideal Fourier Coefficients</strong></td>
</tr>
<tr>
<td>$a_2 = -0.3812$, $b_2 = -0.8523$</td>
</tr>
<tr>
<td><strong>Ellipsometric Parameters</strong></td>
</tr>
<tr>
<td>$\rho = 0.609$, $\Delta = 161.9^\circ$, $\cos(\Delta) = -0.950$</td>
</tr>
<tr>
<td><strong>Refractive Index</strong></td>
</tr>
<tr>
<td>$n = 2.175$, $k = 1.206$</td>
</tr>
</tbody>
</table>

Wobble are lessened for rough surfaces which diffuse the reflected radiation, and therefore, lessen the effects of small beam misalignments caused by polarizer wobble (see Section 6.3.2).

The results shown in Table 7.2 are calculated assuming that the source parameters and window birefringence parameters are known, as shown under given quantities. The calculated quantities are found utilizing the solution methodology.
shown in Figure 3.5, IV. The method used to calculate the source parameters and window birefringence parameters is described in Chapter 3. The source parameters utilized are shown in Figure 3.4 and the birefringence parameters in Chapter 8.

A representative data sheet for each sample material considered is shown in Appendix D. Each data sheet contains information about selected optical components and equipment settings, as well as the intensity measurements.

7.4 Testing — Silicon Wafer Data

As mentioned in the previous section, the high temperature chamber is filled with an inert gas to reduce sample oxidation. The three inert gases considered for this application are helium, argon, and nitrogen. None of the three gases were found to react with the samples in the temperature range of interest (25–600°C). This assessment is based upon results from the procedure used to test for oxidation, which is discussed in the next chapter. Since all three gases were found to be non-reacting, it would be expected that all three gas environments would yield the same results for the high temperature ellipsometry measurements. This is not the case. It is found that each inert gas atmosphere yields the same refractive index at room temperature, but yields different results as the temperature is increased.

In order to resolve this problem with the inert gases, measurements are performed on a silicon wafer sample. The silicon wafer is chosen as the test
sample because the temperature dependence of its refractive index has been previously measured by van der Muelen [56]. Ellipsometric measurements are performed at a wavelength of 633 nm in all three inert gas environments. Because silicon may be considered a dielectric for reflection purposes ($k \approx 0.03$ at room temperature), the imaginary part ($k$) of the refractive index can not be accurately inferred (see Section 6.3.3). The real part ($n$) of the refractive index is found using equation (2.59), which assumes dielectric behavior. The results of the experiment are shown in Figure 7.6 and Table 7.3, and for comparison, the results of van der Muelen are also shown. Because the results in nitrogen were taken after a

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Helium</th>
<th>Argon</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>3.862</td>
<td>3.848</td>
<td>3.798</td>
</tr>
<tr>
<td>200</td>
<td>3.919</td>
<td>4.019</td>
<td>3.934</td>
</tr>
<tr>
<td>300</td>
<td>3.965</td>
<td>4.107</td>
<td>4.015</td>
</tr>
<tr>
<td>400</td>
<td>4.013</td>
<td>4.172</td>
<td>4.084</td>
</tr>
<tr>
<td>500</td>
<td>4.060</td>
<td>4.243</td>
<td>4.135</td>
</tr>
<tr>
<td>600</td>
<td>4.118</td>
<td>4.262</td>
<td>4.170</td>
</tr>
<tr>
<td>700</td>
<td>4.172</td>
<td>4.278</td>
<td>4.203</td>
</tr>
</tbody>
</table>

component realignment, the refractive index values are slightly shifted from the results in other gases. This slight shift of the refractive index is typical when realigning the ellipsometer system, demonstrating the magnitude of the typical
error caused by misalignment. In order to compare the results under different alignment conditions, the percent change of the refractive index with respect to room temperature is shown in Figure 7.7. This figure demonstrates that the results in the helium environment agree with van der Muelen's results, while the trends measured in argon and nitrogen are significantly different. Note that van der Muelen's measurements were performed in a nitrogen environment.

The discrepancies caused by the different inert gas environments may be attributed to the Faraday effect. When a substance exhibiting the Faraday effect is subjected to a magnetic field, it becomes optically active [48]. When a plane-polarized beam of light traverses a path through this optically active medium in a direction parallel to the applied magnetic field, the plane of vibration (polarization) is rotated. The amount of rotation is proportional to the strength of the magnetic field and to the optical pathlength of the medium. The amount of rotation can be expressed as [48, 94–97]

\[ R = VHL \cos (\alpha) \]

where \( R \) is the angle of rotation, \( L \) is the pathlength, \( H \) is the magnetic field strength, \( \alpha \) is the angle between the light beam and lines of force of the magnetic field, and \( V \) is the constant of proportionality known as the Verdet constant. The Verdet constants of the three inert gases used are shown in Table 7.4 [94–96].

The magnetic field in the high temperature chamber is due to the large amount of current (typically 600–1500 amperes) flowing through the resistance
Figure 7.6: Real part (n) of the complex refractive index of a silicon wafer versus temperature at the wavelength $\lambda = 633$ nm measured under three different inert gas environments: helium, nitrogen, and argon. The measured values are compared to those found by van der Muelen [56].
Figure 7.7: The percentage change of the real part ($n$) of the complex refractive index of a silicon wafer with respect to room temperature at the wavelength $\lambda = 633$ nm measured under three different inert gas environments: helium, nitrogen, and argon. The measured values are compared to those found by van der Muelen [56].
heating elements. The current for this experimental system is approximately 600 amperes alternating current at a temperature of 600°C. Comparing Table 7.4 and Figure 7.7, it is seen that the magnitude of the deviation of the measured refractive index of silicon corresponds to the magnitude of the Verdet constant of the inert gas used. These results support the hypothesis that the measured refractive index of a material can be influenced by the Faraday effect occurring in the inert gas environment. Note that because of the silicon-controlled-rectifier (SCR) utilized to control the power into the furnace, the current into the furnace is not true alternating current, but has been rectified somewhat. Therefore, the current flow is always in the same direction. If true alternating current were present, the current direction would reverse 60 times per second. This would probably reduce significantly the consequences of the Faraday effect because the intensity measurement represents an average over several seconds.

One might argue that van der Muelen’s measurements were performed in nitrogen and that these values of refractive index should therefore be in error.
because of the Faraday effect. Because the strength of the magnetic field depends upon the amount of current and the geometry of the current carrying elements, it is not possible to ascertain whether or not the magnetic field strength in van der Muelen's apparatus was similar to that of the present apparatus. It is also possible that van der Muelen's apparatus was utilizing true alternating current, which would tend to negate the consequences of the Faraday effect on the inferred refractive index.

As noted earlier, in the course of the experiments it is found that oxidation of the carbonaceous samples takes place under certain operating conditions. This subject is discussed in the next chapter, along with the birefringence window parameters and the results for the refractive indices of the carbonaceous samples as functions of temperature.
Chapter 8

Results and Discussion

In this chapter, the results of the experimental measurements are presented. The first topic discussed is the method utilized to determine the presence of sample oxidation from experimental measurements. As noted in Chapter 3, it is necessary to determine the birefringence parameters of the windows before inverting the ellipsometric data, and a method for determining the birefringence parameters is presented in Chapter 3. The birefringence parameters found utilizing this technique are presented in Section 8.2 along with a discussion of these parameters. The variation of the refractive index with respect to wavelength and temperature is presented for the three carbonaceous samples considered, which include amorphous carbon, pyrolytic graphite and flame soot. The spectral range considered is the visible region, where the wavelength varies from 400 nm to 700 nm, and the temperature range considered is 25°C–600°C. Following this presentation of results, new parameters for the Drude-Lorentz dispersion model are presented which better represent the materials utilized in this study. In Section 8.5, a
discussion on the experimental results is given and some of the limitations of the 
Drude-Lorentz dispersion model are presented. In this same section, the validity 
of the Clausius–Mossotti equation as it applies to the three carbonaceous sam-
pies is explored. The Clausius–Mossotti equation describes the variation of the 
refractive index with respect to the density of a substance. Finally, the accom-
plishments of this study are summarized and recommendations for future work 
are made.

8.1 Sample Oxidation

Oxygen is a highly reactive gas and will react with many substances, especially at 
high temperatures. Since ellipsometry is a surface technique, the oxidation of the 
sample surface will greatly influence the measured ellipsometric parameters, and 
therefore the inferred complex refractive index. The objective of this research is 
to evaluate the effect of temperature on the refractive index, while holding all 
other parameters constant. Therefore, it is necessary to greatly reduce or elimi-
nate sample oxidation. In order to reduce sample oxidation, the high temperature 
chamber is purged and filled with an inert gas. Because it is impossible to remove 
all oxygen, oxidation is still seen to occur at high temperatures. The onset of 
significant oxidation occurs at a temperature of approximately 700–800°C for all 
samples tested. The presence of oxidation is detected by measuring the complex 
refractive index during a heating/cooling cycle. If the complex refractive index 
measurements for the heating part of the cycle are the same as for the cooling
part of the cycle, the sample has undergone no detectable oxidation. Figure 8.1 shows the results of such a measurement on an amorphous carbon sample. It is seen in the upper graph of Figure 8.1 that significant oxidation has taken place when the sample was heated to a temperature of 1200°C, while in the lower graph of Figure 8.1, it is seen that the sample undergoes no noticeable oxidation when heated to a temperature of 600°C. Similar results were obtained for all samples tested, including the silicon wafer. The three carbonaceous samples were found to have an oxidation threshold of approximately 700°C, while the oxidation threshold of the silicon wafer was found to be approximately 800°C. Therefore, the maximum temperatures utilized for this study are 600°C for the carbonaceous samples and 700°C for the silicon wafer.

8.2 Window Birefringence Parameters

The equations presented in Chapter 3 describe how to measure the birefringence parameters of the windows ($\alpha_1$, $\beta_1$, $\alpha_2$, and $\beta_2$), utilizing measurements taken from a reflecting sample. These birefringence parameters are properties of the windows only and should be independent of the properties of the reflecting sample. In reality, the measured birefringence parameters do depend upon the reflecting sample. The possible reasons for this are: (i) the small wave retardation plate (SWRP) approximation used to model the windows may not be completely valid, and (ii) the reflected beam may pass through a different part of the window when the ellipsometer is aligned to accommodate a new sample.
Figure 8.1: Refractive index of oxidized and un-oxidized amorphous carbon. Real ($n$) and imaginary ($k$) parts of the complex refractive index of amorphous carbon shown as functions of temperature at the wavelength $\lambda = 488$ nm. Significant oxidation has occurred in the upper graph but not in the lower graph.
This different part of the window may have different levels of stress, resulting in different birefringence parameters.

The SWRP approximation assumes that the windows of the ellipsometer system act as linear retarders (see Section 3.5) with small amounts of retardation. If the birefringence of the windows becomes large, it may become necessary to include all terms in the linear retarder Mueller matrix. A pure retarder is also assumed to have a transmission ratio of 1, meaning that the fraction of light transmitted is independent of the direction of polarization. If the transmission ratio of the window is not actually 1, the Mueller matrix of the window should be further modified. Furthermore, the window may not be a pure linear retarder, but could be an elliptical (most general) retarder. Once again, this will change the Mueller matrix of the window.

As mentioned in Section 3.5, the windows have some effect on beam polarization, with this effect being described by their Mueller matrices, \( [W_1] \) and \( [W_2] \). The birefringence parameters of the windows (\( \alpha_1, \beta_1, \alpha_2, \) and \( \beta_2 \)) are calculated from the experimental Fourier coefficients as explained in Section 3.5. As noted earlier, the birefringence parameters determined from this technique are dependent upon the material used for the reflection sample. Therefore, the amorphous carbon plate and the soot pellet were utilized as reflection samples to determine the birefringence parameters of the windows. The pyrolytic graphite sample was also utilized as a reflection sample, but it was found that the measured
window birefringence parameters are approximately equal to the window parameters found using amorphous carbon as the reflecting sample.

The window parameters found with an amorphous carbon sample are shown in Table 8.1 and Figure 8.2. The window parameters found with a soot pellet sample are shown in Table 8.2 and Figure 8.3. It is seen that the measured window parameters are indeed dependent upon the sample utilized, and the possible reasons for this have been noted. It is also seen that the window parameters approximately fit an inverse wavelength curve (shown with a dark line in Figures 8.2–8.3), with the deviation of the data from this inverse wavelength curve caused by dispersion of the stress optic coefficient and, to some extent,

Table 8.1: Window birefringence parameters – Reflection sample: Amorphous carbon.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>α₁</th>
<th>β₁</th>
<th>α₂</th>
<th>β₂</th>
</tr>
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<tr>
<td>400</td>
<td>-26.12</td>
<td>-9.22</td>
<td>1.22</td>
<td>-3.68</td>
</tr>
<tr>
<td>433</td>
<td>-25.43</td>
<td>-8.97</td>
<td>1.50</td>
<td>-3.45</td>
</tr>
<tr>
<td>467</td>
<td>-24.13</td>
<td>-9.04</td>
<td>2.05</td>
<td>-3.11</td>
</tr>
<tr>
<td>500</td>
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<td>-8.25</td>
<td>2.03</td>
<td>-2.48</td>
</tr>
<tr>
<td>533</td>
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<td>567</td>
<td>-17.21</td>
<td>-6.29</td>
<td>1.95</td>
<td>-2.29</td>
</tr>
<tr>
<td>600</td>
<td>-15.39</td>
<td>-5.50</td>
<td>1.47</td>
<td>-2.20</td>
</tr>
<tr>
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<td>-5.57</td>
<td>1.81</td>
<td>-1.42</td>
</tr>
<tr>
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<td>1.84</td>
<td>-1.13</td>
</tr>
<tr>
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<td>-12.55</td>
<td>-5.67</td>
<td>2.02</td>
<td>-1.70</td>
</tr>
</tbody>
</table>
Figure 8.2: The birefringence parameters of the entrance (upper graph) and exit (lower graph) windows found utilizing amorphous carbon as the reflection sample. The heavy curve represents the fit of the data to an inverse wavelength function.
Figure 8.3: The birefringence parameters of the entrance (upper graph) and exit (lower graph) windows found utilizing a soot pellet as the reflection sample. The heavy curve represents the fit of the data to an inverse wavelength function.
Table 8.2: Window birefringence parameters – Reflection sample: Soot pellet.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>( \alpha_1 )</th>
<th>( \beta_1 )</th>
<th>( \alpha_2 )</th>
<th>( \beta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>-11.81</td>
<td>-11.53</td>
<td>1.07</td>
<td>-9.69</td>
</tr>
<tr>
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<td>-10.86</td>
<td>1.09</td>
<td>-9.30</td>
</tr>
<tr>
<td>467</td>
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<td>-10.06</td>
<td>0.95</td>
<td>-9.16</td>
</tr>
<tr>
<td>500</td>
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<td>-9.45</td>
<td>1.06</td>
<td>-8.54</td>
</tr>
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<td>0.78</td>
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<td>-8.11</td>
<td>1.00</td>
<td>-7.11</td>
</tr>
<tr>
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<td>-7.01</td>
<td>1.97</td>
<td>-6.49</td>
</tr>
<tr>
<td>633</td>
<td>-7.85</td>
<td>-6.03</td>
<td>-0.54</td>
<td>-7.03</td>
</tr>
<tr>
<td>667</td>
<td>-6.67</td>
<td>-6.29</td>
<td>0.11</td>
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<td>-7.03</td>
<td>-5.72</td>
<td>0.14</td>
<td>-6.20</td>
</tr>
</tbody>
</table>

experimental error. The curves shown by dark lines in Figures 8.2–8.3 are of the form \( C/\lambda \), where \( C \) is a constant found by a least squares fit of the data.

### 8.3 Refractive Indices of Carbonaceous Samples

The refractive indices inferred from ellipsometry measurements are presented in this section (§8.3). As noted earlier, the three materials considered in this study include amorphous carbon, pyrolytic graphite and flame soot. The values measured in this study are compared to the Drude-Lorentz dispersion model, which is described in Chapter 1. This dispersion model has been used by other investigators to predict the refractive indices of carbonaceous materials.
8.3.1 Amorphous Carbon

The measured refractive index for amorphous carbon is shown in Figure 8.4 for the temperatures 25°C, 200°C, 400°C, and 600°C in the wavelength range 400–700 nm. The experimental values shown in this figure are tabulated in Table 8.3.

From Figure 8.4, it is seen that the measured refractive index varies imperceptibly with temperature. In other words, the changes seen with respect to temperature are within the experimental error bounds of this technique (see Section 6.4). The predictions of the Drude-Lorentz dispersion model are shown by the heavy solid lines. In Figure 8.5, the percentage deviation of the measured refractive index with respect to room temperature (25°C) is compared to the predictions of the

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>T = 25°C</th>
<th>T = 200°C</th>
<th>T = 400°C</th>
<th>T = 600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>k</td>
<td>n</td>
<td>k</td>
</tr>
<tr>
<td>400</td>
<td>2.175</td>
<td>1.206</td>
<td>2.176</td>
<td>1.216</td>
</tr>
<tr>
<td>433</td>
<td>2.258</td>
<td>1.102</td>
<td>2.272</td>
<td>1.099</td>
</tr>
<tr>
<td>467</td>
<td>2.323</td>
<td>1.025</td>
<td>2.330</td>
<td>1.019</td>
</tr>
<tr>
<td>500</td>
<td>2.321</td>
<td>0.991</td>
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<td>1.987</td>
</tr>
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<td>2.331</td>
<td>0.981</td>
<td>2.343</td>
<td>1.978</td>
</tr>
<tr>
<td>567</td>
<td>2.337</td>
<td>0.977</td>
<td>2.247</td>
<td>1.969</td>
</tr>
<tr>
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<td>2.343</td>
<td>0.982</td>
<td>2.353</td>
<td>1.975</td>
</tr>
<tr>
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<td>2.356</td>
<td>0.986</td>
<td>2.361</td>
<td>1.974</td>
</tr>
<tr>
<td>667</td>
<td>2.371</td>
<td>1.019</td>
<td>2.362</td>
<td>1.031</td>
</tr>
<tr>
<td>700</td>
<td>2.434</td>
<td>1.005</td>
<td>2.436</td>
<td>1.009</td>
</tr>
</tbody>
</table>
Figure 8.4: The real ($n$) and imaginary ($k$) parts of the complex refractive index of amorphous carbon for the temperatures $25^\circ C$, $200^\circ C$, $400^\circ C$, and $600^\circ C$. The smooth curves with no data points are predictions of the Drude–Lorentz model.
Figure 8.5: The percentage change of the real part (upper graph), $n$, and imaginary part (lower graph), $k$, of the complex refractive index of amorphous carbon with respect to room temperature ($25°C$) for the temperatures $200°C$, $400°C$, and $600°C$. The smooth curves with no data points are predictions of the Drude–Lorentz model.
Drude-Lorentz dispersion model. In both Figures 8.4 and 8.5, it is seen that this dispersion model predicts a relatively large change (up to 30 percent) with respect to temperature, whereas the measured values of refractive index exhibit no measurable change with respect to temperature.

8.3.2 Pyrolytic Graphite

The measured refractive index for pyrolytic graphite is shown in Figure 8.6 for the temperatures 25°C, 200°C, 400°C, and 600°C and the experimental values are tabulated in Table 8.4. The behavior of the optical properties of this material

<table>
<thead>
<tr>
<th>Table 8.4: Refractive index of pyrolytic graphite.</th>
</tr>
</thead>
</table>
| \[ \begin{array}{|c|c|c|c|c|c|c|c|}
| \hline
| \( \lambda \) (nm) & \( T = 25°C \) & \( T = 200°C \) & \( T = 400°C \) & \( T = 600°C \) \\
| \hline
| 433 & 2.529 & 1.528 & 2.544 & 1.508 & 2.562 & 1.515 & 2.555 & 1.525 \\
| 600 & 2.656 & 1.394 & 2.674 & 1.394 & 2.695 & 1.379 & 2.691 & 1.385 \\
| 667 & 2.717 & 1.433 & 2.741 & 1.431 & 2.731 & 1.428 & 2.733 & 1.418 \\
| \hline
| \end{array} \] |

with respect to temperature is similar to that of amorphous carbon, with the refractive index showing no measurable temperature dependence. The percentage
Figure 8.6: The real ($n$) and imaginary ($k$) parts of the complex refractive index of pyrolytic graphite for the temperatures 25°C, 200°C, 400°C, and 600°C. The smooth curves with no data points are predictions of the Drude–Lorentz model.
Figure 8.7: The percentage change of the real part (upper graph), \( n \), and the imaginary part (lower curve), \( k \), of the complex refractive index of pyrolytic graphite with respect to room temperature \((25^\circ C)\) for the temperatures \(200^\circ C\), \(400^\circ C\), and \(600^\circ C\). The smooth curves with no data points are predictions of the Drude–Lorentz model.
change of the refractive index with respect to room temperature is shown in Figure 8.7. Once again, the predictions of the Drude-Lorentz dispersion model are compared to the experimentally measured values in Figures 8.6–8.7.

### 8.3.3 Soot Pellet

The measured refractive index of the soot pellet is shown in Figure 8.8 for the temperatures 25°C, 300°C, and 600°C and the values are tabulated in Table 8.5. The refractive index of this material is seen to be essentially independent of temperature as shown in Figure 8.9.

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>T = 25°C</th>
<th>T = 300°C</th>
<th>T = 600°C</th>
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</thead>
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<td></td>
<td>n</td>
<td>k</td>
<td>n</td>
</tr>
<tr>
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<td>1.396</td>
<td>0.403</td>
<td>1.392</td>
</tr>
<tr>
<td>433</td>
<td>1.434</td>
<td>0.376</td>
<td>1.431</td>
</tr>
<tr>
<td>467</td>
<td>1.462</td>
<td>0.360</td>
<td>1.464</td>
</tr>
<tr>
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<td>1.484</td>
<td>0.347</td>
<td>1.482</td>
</tr>
<tr>
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<td>1.494</td>
</tr>
<tr>
<td>567</td>
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<td>0.374</td>
<td>1.537</td>
</tr>
<tr>
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<td>0.355</td>
<td>1.521</td>
</tr>
<tr>
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<td>0.376</td>
<td>1.529</td>
</tr>
<tr>
<td>667</td>
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<td>0.357</td>
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</tr>
<tr>
<td>700</td>
<td>1.550</td>
<td>0.367</td>
<td>1.548</td>
</tr>
</tbody>
</table>

Table 8.5: Refractive index of propane soot pellet.
Figure 8.8: The real ($n$) and imaginary ($k$) parts of the complex refractive index of flame soot for the temperatures 25°C, 300°C and 600°C. The smooth curves with no data points are predictions of the Drude–Lorentz model.
Figure 8.9: The percentage change of the real part (upper graph), \( n \) and imaginary part (lower graph), \( k \), of the complex refractive index of flame soot with respect to room temperature (25°C) for the temperatures 300°C and 600°C. The smooth curves with no data points are predictions of the Drude–Lorentz model.
8.4 Drude-Lorentz Parameters

In the preceding section, the predictions of the Drude-Lorentz dispersion model were compared to experimentally determined values. It was seen that this dispersion model failed to predict the variation of the experimentally determined refractive index with respect to both wavelength and temperature. As mentioned in Chapter 1, the Drude-Lorentz model considers the solid to be an assembly of oscillators (electrons) which are set into forced vibration by the incident radiation. Each oscillator has an associated damping constant \((g)\) and a resonant frequency \((\omega_0)\). The free (conduction) electrons have a resonant frequency of zero. The number density and damping constants of the electrons in this model can be altered to force the model to fit the experimental values. The same procedure was adopted by Lee and Tien [8] and Charalampopoulos and Chang [13].

As noted in Chapter 1, previous investigators [8,31,32] assumed that the damping constants changed with temperature in order to predict the variation of the refractive index with respect to temperature. The results of this study indicate that the refractive index of the carbonaceous materials considered are independent of temperature (within the temperature and spectral ranges considered) and that the refractive index determined at any temperature is representative for all temperatures. Therefore, it is only necessary to calculate the Drude-Lorentz dispersion parameters at one temperature and assume that these parameters are valid at all temperatures.
The dispersion model for carbonaceous materials assumes that the material is composed of two types of bound electrons and one free electron. Each bound electron has an associated number density, natural frequency and damping constant. The quantities associated with the free electrons are number density and damping constant since the natural frequency is zero. With these assumptions, there are eight dispersion parameters for the Drude-Lorentz dispersion model when it is applied to carbonaceous materials. Soot and amorphous carbon are assumed to possess the same optical transitions as those of graphite, meaning that its electrons have the same resonant frequencies as graphite. With this assumption, the resonant frequencies, $\omega_{b,1}$ and $\omega_{b,2}$, take the values shown in Table 1.1. The damping constant of the free electrons is also assumed constant with its value shown in Table 1.1. Furthermore, a relation is assumed between the number densities of the electrons [8,13], and is given as

$$n_{b,2} = 11n_{b,1} - n_f .$$  \hspace{1cm} (8.1)

Therefore, only four dispersion parameters $(n_f, n_{b,1}, g_{b,1}, g_{b,2})$ remain to be determined. These four parameters are found by minimizing the function

$$F = \sum_{i=1}^{N} \left[ (n_{th,i} - n_{exp,i})^2 + (k_{th,i} - k_{exp,i})^2 \right] ,$$  \hspace{1cm} (8.2)

where the subscript $th$ represents the predictions of the dispersion model, the subscript $exp$ represents the experimentally determined value at room temperature, and $N$ is the number of experimental data points ($N = 10$ for these
calculations). The dispersion parameters found for the three carbonaceous samples are tabulated in Tables 8.6-8.8.

Table 8.6: Dispersion constants for amorphous carbon.

<table>
<thead>
<tr>
<th>Type of Electron</th>
<th>Electron number density $m^{-3} \times 10^{-25}$</th>
<th>Frequency $\omega \times 10^{-15}\text{sec}^{-1}$</th>
<th>Damping constant $g \times 10^{-15}\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free:</td>
<td>0.041</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>Bound 1:</td>
<td>831</td>
<td>1.25</td>
<td>3.5</td>
</tr>
<tr>
<td>Bound 2:</td>
<td>9140</td>
<td>7.25</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Table 8.7: Dispersion constants for pyrolytic graphite.

<table>
<thead>
<tr>
<th>Type of Electron</th>
<th>Electron number density $m^{-3} \times 10^{-25}$</th>
<th>Frequency $\omega \times 10^{-15}\text{sec}^{-1}$</th>
<th>Damping constant $g \times 10^{-15}\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free:</td>
<td>26.3</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>Bound 1:</td>
<td>1310</td>
<td>1.25</td>
<td>6.3</td>
</tr>
<tr>
<td>Bound 2:</td>
<td>14400</td>
<td>7.25</td>
<td>11.2</td>
</tr>
</tbody>
</table>
Table 8.8: Dispersion constants for flame soot.

<table>
<thead>
<tr>
<th>Type of Electron</th>
<th>Electron number density $m^{-3} \times 10^{-25}$</th>
<th>Frequency $\omega \times 10^{-15} \text{sec}^{-1}$</th>
<th>Damping constant $g \times 10^{-18} \text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free:</td>
<td>0.14</td>
<td>–</td>
<td>1.2</td>
</tr>
<tr>
<td>Bound 1:</td>
<td>216</td>
<td>1.25</td>
<td>9.8</td>
</tr>
<tr>
<td>Bound 2:</td>
<td>2380</td>
<td>7.25</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The agreement between the experimentally determined values and the predictions of the dispersion model utilizing the new dispersion constants is shown in Figures 8.10–8.12. It should be noted that since these dispersion parameters were determined with data which covers a limited spectral range (400 nm – 700 nm), the new parameters may not be valid outside of the visible spectrum.
Figure 8.10: Refractive index of amorphous carbon compared to the Drude-Lorentz model utilizing the parameters shown in Table 8.6.
Figure 8.11: Refractive index of pyrolytic graphite compared to the Drude-Lorentz model utilizing the parameters shown in Table 8.7.
Figure 8.12: Refractive index of flame soot compared to the Drude-Lorentz model utilizing the parameters shown in Table 8.8.
8.5 Discussion

The purpose of this study is to experimentally evaluate the temperature dependence of the refractive index of carbonaceous materials and to compare this measured temperature dependence with the predictions of the available dispersion models. The Drude-Lorentz dispersion model (see Chapter 1) has been frequently utilized to model the wavelength dependence of the optical properties of many materials. Lee and Tien [8] proposed that some of the parameters of the dispersion equations (namely, the damping constants of the electrons) vary with temperature, which would force the refractive index of the material to vary with temperature. Specifically, Lee and Tien [8] stated that the damping constants of the electrons are proportional to the square root of temperature.

It should be noted that the Drude-Lorentz model is a simplistic model with foundations in classical physics. A rigorous description of the optical properties of a material requires the application of quantum mechanics. Nevertheless, the Drude-Lorentz model does describe the general features of the optical properties of many materials, but it may not describe all of the details of these optical properties [47]. In the preceding section of this chapter (§8.4), the Drude-Lorentz model was treated somewhat empirically, with the dispersion parameters being modified so that the equations fit the experimental results.

In the course of this study, it was found that the optical properties (complex refractive index) of the carbonaceous materials studied do not vary with
temperature in the wavelength and temperature ranges considered. This does not imply that the refractive index of carbonaceous materials is completely independent of temperature at other values of wavelength and temperature. The temperature and spectral ranges evaluated in this study are 25–600°C and 400–700 nm, respectively. It is stated by Bohren and Huffman [47] that, in general, temperature more greatly affects low-frequency than high-frequency absorption mechanisms. Therefore, the refractive indices of carbonaceous materials may be more greatly affected at infrared wavelengths than at the visible wavelengths studied. The infrared wavelengths were excluded from this study because of the poor sensitivity of the ellipsometry technique at these wavelengths due to low polarizer quality and small angle of incidence (see Chapter 5). Bohren and Huffman [47] also state that absorption in amorphous solids tends to be independent of temperature, but that the far-infrared absorption in crystalline solids may change by several orders of magnitude as temperature increases. From this statement, it is expected that the optical properties of amorphous carbon and flame soot (both amorphous materials) would be independent of temperature, but that the optical properties of pyrolytic graphite may be more sensitive to changes in temperature, since pyrolytic graphite approaches crystalline behavior [64]. This is not the behavior observed in this study, and, in fact, the optical properties of all three carbonaceous samples are seen to be virtually independent of temperature. Once again, this does not imply that the observed temperature
independence will hold for all temperature ranges and spectral regions. What may be concluded from this study is that Lee and Tien's [8] assumed square root temperature dependence assigned to the damping constants of the electrons is incorrect. More specifically, it can be said that the damping constants of the electrons are independent of temperature for the materials and conditions specified in this study. This fact was stated in the preceding section (§8.4), where the dispersion parameters were inferred from room temperature results and were said to be valid over the temperature range 25-600°C.

A second interesting aspect of the experimental data is the variation of refractive index from sample to sample. Although all three samples are composed mostly of carbon, the optical properties of each sample are significantly different. Comparing Tables 8.3-8.5, it is seen that the magnitudes of the real and imaginary parts of the refractive index are seen to be largest for the materials with the greatest density. The densities of the three carbonaceous samples, shown in Table 8.9, were determined from the measured weights and volumes of the bulk samples. The volume was computed from the measured linear dimensions of the bulk sample, knowing the shape of the sample, and the weight was measured on a precision balance.

It has been stated by Ku and Shim [98] that since all soot and carbon black particles have the same turbostratic graphitic microstructure but with different mass densities, their complex refractive indices could be modelled by
the Clausius-Mossotti formula. The Clausius-Mossotti (C–M) equation is given as [98]

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{\rho}{\rho_{\text{reference}}} \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right)_{\text{reference}},$$

where $\varepsilon$ is the complex dielectric function, $\rho$ is the density and the subscript reference represents the quantities of a known reference material. The complex dielectric function is given in terms of the complex refractive index as

$$\varepsilon = (n - ik)^2.$$  \hfill (8.4)

The C–M equation has been successfully used to model the refractive index of gases under different pressures [99] (or equivalently, different densities). Gases are essentially transparent and therefore have a real refractive index ($k = 0$). Although the three carbonaceous samples utilized for this study do not have the same structure, it is of interest to evaluate the validity of the C–M equation as it is applied to these three samples.
To test the equation, the density of a given sample is calculated from its experimentally determined refractive index as

\[
\rho = \rho_{\text{reference}} \frac{(\varepsilon - 1)}{(\varepsilon + 2)} / \frac{(\varepsilon - 1)}{(\varepsilon + 2)}_{\text{reference}},
\]

where pyrolytic graphite was chosen as the reference sample (\(\rho_{\text{reference}} = 2.2 \text{ g/cm}^3\)). Because the experimentally determined refractive index has been found at different wavelengths, the calculations of equation (8.5) can be performed at different wavelengths. The interesting fact about equation (8.5) is that the density predicted by this equation will be complex since \(\varepsilon\) is complex. The results of the computation of equation (8.5) are shown in Table 8.10. Of course, a complex density is physically meaningless, but the real part of the

<table>
<thead>
<tr>
<th>(\lambda) (nm)</th>
<th>(\text{Re}(\rho))</th>
<th>(\text{Im}(\rho))</th>
<th>(\text{Re}(\rho))</th>
<th>(\text{Im}(\rho))</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.82</td>
<td>0.30</td>
<td>1.93</td>
<td>0.12</td>
</tr>
<tr>
<td>433</td>
<td>0.86</td>
<td>0.28</td>
<td>1.94</td>
<td>0.11</td>
</tr>
<tr>
<td>467</td>
<td>0.90</td>
<td>0.26</td>
<td>1.94</td>
<td>0.10</td>
</tr>
<tr>
<td>500</td>
<td>0.92</td>
<td>0.24</td>
<td>1.94</td>
<td>0.10</td>
</tr>
<tr>
<td>533</td>
<td>0.94</td>
<td>0.24</td>
<td>1.94</td>
<td>0.09</td>
</tr>
<tr>
<td>567</td>
<td>1.00</td>
<td>0.23</td>
<td>1.93</td>
<td>0.09</td>
</tr>
<tr>
<td>600</td>
<td>0.97</td>
<td>0.22</td>
<td>1.93</td>
<td>0.09</td>
</tr>
<tr>
<td>633</td>
<td>0.98</td>
<td>0.25</td>
<td>1.94</td>
<td>0.09</td>
</tr>
<tr>
<td>667</td>
<td>0.98</td>
<td>0.22</td>
<td>1.94</td>
<td>0.10</td>
</tr>
<tr>
<td>700</td>
<td>0.99</td>
<td>0.23</td>
<td>1.95</td>
<td>0.08</td>
</tr>
</tbody>
</table>
density, \( Re(\rho) \), shown in Table 8.10 does correspond, within 15–20 percent, to the experimentally determined sample densities. It should also be noted that the density is not a function of wavelength, and the variation shown with wavelength in Table 8.10 is simply a failure of the C–M equation.

The C–M equation was used by Ku and Shim [98] to predict the complex refractive index of a material and not the density. Equation (8.3) can be utilized to calculate the complex refractive index \((n - ik)\) if the density of the sample is known and the density and complex refractive index of a reference sample are known. This calculation was carried out using pyrolytic graphite as the reference sample and the results are shown in Tables 8.11–8.12. In these tables the experimentally determined refractive indices are compared to the refractive indices predicted by the C–M equation (subscript \( CM \)).

From Tables 8.11–8.12, it is seen that the real part of the refractive index predicted by the C–M equation is within 5–10 percent of the experimentally determined values, but the imaginary part of the refractive index predicted by the C–M equation may differ by 60 percent from the experimentally determined values. From the results in Tables 8.10–8.12, it can be concluded that the Clausius–Mossotti equation is not strictly valid for the three carbonaceous samples tested, but does predict the general trends of the experimental results.
Table 8.11: Refractive index of amorphous carbon predicted by the Clau-\sius-Mossotti equation.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$n_{\text{exp}}$</th>
<th>$n_{\text{CM}}$</th>
<th>$k_{\text{exp}}$</th>
<th>$k_{\text{CM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2.175</td>
<td>2.304 (5.9)*</td>
<td>1.206</td>
<td>1.018 (-15.6)*</td>
</tr>
<tr>
<td>433</td>
<td>2.258</td>
<td>2.347 (4.0)</td>
<td>1.102</td>
<td>0.894 (-18.9)</td>
</tr>
<tr>
<td>467</td>
<td>2.323</td>
<td>2.375 (2.2)</td>
<td>1.025</td>
<td>0.804 (-21.6)</td>
</tr>
<tr>
<td>500</td>
<td>2.321</td>
<td>2.367 (2.0)</td>
<td>0.991</td>
<td>0.784 (-20.9)</td>
</tr>
<tr>
<td>533</td>
<td>2.331</td>
<td>2.370 (1.7)</td>
<td>0.981</td>
<td>0.780 (-20.5)</td>
</tr>
<tr>
<td>567</td>
<td>2.337</td>
<td>2.374 (1.6)</td>
<td>0.977</td>
<td>0.786 (-19.5)</td>
</tr>
<tr>
<td>600</td>
<td>2.343</td>
<td>2.377 (1.5)</td>
<td>0.982</td>
<td>0.784 (-20.2)</td>
</tr>
<tr>
<td>633</td>
<td>2.356</td>
<td>2.394 (1.6)</td>
<td>0.986</td>
<td>0.779 (-21.0)</td>
</tr>
<tr>
<td>667</td>
<td>2.371</td>
<td>2.321 (2.1)</td>
<td>1.019</td>
<td>0.787 (-22.7)</td>
</tr>
<tr>
<td>700</td>
<td>2.434</td>
<td>2.345 (0.6)</td>
<td>1.005</td>
<td>0.776 (-22.8)</td>
</tr>
<tr>
<td><strong>Average differences (%)</strong></td>
<td><strong>2.3</strong></td>
<td></td>
<td><strong>20.4</strong></td>
<td></td>
</tr>
</tbody>
</table>

* Numbers in parenthesis represent percent differences between the experimental values of $n$ and $k$ and those predicted by the C–M equation.
Table 8.12: Refractive index of flame soot predicted by the Clausius-Mossotti equation.

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$n_{\text{exp}}$</th>
<th>$n_{\text{CM}}$</th>
<th>$k_{\text{exp}}$</th>
<th>$k_{\text{CM}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>1.396</td>
<td>1.528 (9.5)*</td>
<td>0.403</td>
<td>0.215 (-46.6)*</td>
</tr>
<tr>
<td>433</td>
<td>1.434</td>
<td>1.519 (5.9)</td>
<td>0.376</td>
<td>0.187 (-50.3)</td>
</tr>
<tr>
<td>467</td>
<td>1.462</td>
<td>1.513 (3.5)</td>
<td>0.360</td>
<td>0.167 (-53.6)</td>
</tr>
<tr>
<td>500</td>
<td>1.484</td>
<td>1.509 (1.7)</td>
<td>0.347</td>
<td>0.164 (-52.7)</td>
</tr>
<tr>
<td>533</td>
<td>1.496</td>
<td>1.509 (0.9)</td>
<td>0.352</td>
<td>0.163 (-53.7)</td>
</tr>
<tr>
<td>567</td>
<td>1.536</td>
<td>1.511 (-1.7)</td>
<td>0.374</td>
<td>0.164 (-56.2)</td>
</tr>
<tr>
<td>600</td>
<td>1.522</td>
<td>1.511 (-0.7)</td>
<td>0.355</td>
<td>0.163 (-54.1)</td>
</tr>
<tr>
<td>633</td>
<td>1.527</td>
<td>1.514 (-0.9)</td>
<td>0.376</td>
<td>0.160 (-57.4)</td>
</tr>
<tr>
<td>667</td>
<td>1.544</td>
<td>1.519 (-1.6)</td>
<td>0.357</td>
<td>0.159 (-55.5)</td>
</tr>
<tr>
<td>700</td>
<td>1.550</td>
<td>1.523 (-1.7)</td>
<td>0.367</td>
<td>0.154 (-58.0)</td>
</tr>
</tbody>
</table>

Average differences (%): 2.8 53.8

* Numbers in parenthesis represent percent differences between the experimental values of $n$ and $k$ and those predicted by the C–M equation.
8.6 Summary

A technique for determining the temperature dependence of the refractive index was developed in this study. The refractive index was found from the measured Fourier coefficients of a PSA ellipsometer. This study also assessed the effects of cell window birefringence on the measured refractive index. A method was presented to calculate the window birefringence parameters and then these parameters were used to calculate the true refractive index of the sample.

The refractive indices of three carbonaceous materials (amorphous carbon, pyrolytic graphite, and flame soot) were measured over the temperature range 25–600°C and the spectral range 400–700 nm. It was seen that for all three of these materials, the measured refractive index showed insignificant temperature dependence. These results differ greatly from the predictions of the Drude-Lorentz dispersion model, although this model has been used extensively to predict the temperature and wavelength dependence of the optical properties of carbonaceous particulates.
8.7 Recommendations and Future Work

In this section, recommendations will be made concerning improvements to the experimental apparatus and technique. Some possible directions for future work will also be listed. The recommendations for improvements are divided into two categories: (i) improvements related to the optical system and (ii) improvements related to the high temperature furnace unit.

**Improvements Related to the Optical System**

1. Increase the angle of incidence to approximately 70 degrees. This would increase the numerical sensitivity (see Chapter 5) of the data inversion. A precisely adjustable angle of incidence would allow the system to be tailored for a specific material, but this is not feasible for a high temperature unit such as the one utilized in this study.

2. Add a compensator to the optical system, placing it in the beam path just after the polarizer. This would also increase the sensitivity of the experimental technique. The disadvantage of this component is that the compensator must be precisely calibrated at each wavelength of interest. Therefore, the addition of this component could actually decrease accuracy if the element is not correctly calibrated.
3. Consider adding a diffuser to the optical system just before the entrance to the monochromator. This will minimize the effects of small beam misalignments and polarizer wobble. The disadvantage of this component is that the intensity reaching the detector will be decreased, which will in turn decrease the signal-to-noise ratio.

4. Increase the intensity of the light source. This will increase the signal-to-noise ratio and will offset the problems caused by the addition of a diffuser.

5. Add a high intensity, infrared source to the optical system. This will allow measurements to be performed at longer wavelengths.

6. Automate the data acquisition system. The ellipsometry technique requires a large number of experimental measurements to evaluate the refractive index at one wavelength and one temperature. Therefore, the evaluation of the refractive index for multiple samples at multiple wavelengths and temperatures is a very tedious procedure. To automate the process, the polarizer is rotated at a precisely controlled speed and the intensity is measured at equally spaced time intervals (see for example [56,93,100–101]). This technique allows data acquisition at high rates and also allows many more experimental measurements per polarizer revolution, which will decrease the experimental error.
**Improvements Related to the Furnace Unit**

1. Investigate the possibility of annealing the furnace windows to lessen their birefringence. If the birefringence cannot be decreased to an acceptable level, the full Mueller matrix of each window should be determined. This will require the use of a transmission ellipsometer.

2. Improve the vacuum capabilities of the furnace chamber. This will decrease sample oxidation and allow higher temperatures to be investigated.

3. Devise a sample holder that aligns the sample surface in a fixed location and orientation. This would eliminate the need to realign the optical components and sample holder for each sample and would allow more repeatable results from sample to sample.

4. Mount the thermocouple in a location that senses the temperature of the center of the hot zone but does not interfere with the beam.
Future Work

1. Investigate the optical properties of the carbonaceous samples at other wavelengths. As stated earlier in this Chapter, the optical properties of materials may be more sensitive to temperature at lower frequencies (longer wavelengths).

2. Investigate the optical properties of the carbonaceous samples at other temperatures. If the presence of oxidation can be eliminated, the optical properties can be investigated at temperatures as high as 2300°C. Also, the optical properties of carbonaceous materials at very low temperatures (approaching absolute zero) is of interest to astronomers because carbon is thought to be a primary constituent of the interstellar dust [102]. Measurements at temperatures below room temperature are not possible on the present experimental apparatus.

3. The optical properties of other materials at elevated temperatures is also of interest. For example, aluminum oxide is produced in the exhaust of some solid-fueled rocket boosters. Therefore, the knowledge of the optical properties of this material is required when performing radiative transfer calculations or performing optical diagnostics on the rocket exhaust.
Bibliography


Appendix A

Common Mueller Matrices

Various Mueller matrices were utilized throughout this report. Some of the common Mueller matrices will be given in this appendix.

The Mueller matrix of an ideal polarizer is given as \[33,41\]

\[
[P] = \frac{k_1}{2} \begin{bmatrix}
1 & \cos(2P) & \sin(2P) & 0 \\
\cos(2P) & \cos^2(2P) & \sin(2P)\cos(2P) & 0 \\
\sin(2P) & \sin(2P)\cos(2P) & \sin^2(2P) & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}.
\] (A.1)

where \(k_1\) is the principal transmittance of the polarizer and \(P\) represents the azimuthal angle between the transmission axis of the polarizer and some reference plane. The analyzer is simply a polarizing element and its Mueller matrix is given by equation (A.1).

The Mueller matrix of a linear retarder, \([Q]\), was utilized to describe the effects of birefringent cell windows, and is given as \[58\]

\[
[Q] = \begin{bmatrix}
1 & 0 & 0 & 0 \\
0 & c^2 + s^2\cos(\delta) & sc(1 - \cos(\delta)) & -s\sin(\delta) \\
0 & sc(1 - \cos(\delta)) & s^2 + c^2\cos(\delta) & c\sin(\delta) \\
0 & s\sin(\delta) & -c\sin(\delta) & \cos(\delta)
\end{bmatrix},
\] (A.2)

where

\[
s = \sin(2\theta)
\] (A.3)
and
\[ c = \cos(2\theta). \quad (A.4) \]

In equations (A.2)-(A.4), \( \theta \) is the azimuthal angle between the fast axis and the reference plane and \( \delta \) is the amount of retardation.

The Mueller matrix representing reflection from a sample, \([S]\), with ellipsometric parameters \( \rho \) and \( \Delta \) and may be written as \([33,41]\)
\[ [S] = \frac{R_\perp}{2} \begin{bmatrix} \rho^2 + 1 & \rho^2 - 1 & 0 & 0 \\ \rho^2 - 1 & \rho^2 + 1 & 0 & 0 \\ 0 & 0 & 2\rho \cos \Delta & 2\rho \sin \Delta \\ 0 & 0 & -2\rho \sin \Delta & 2\rho \cos \Delta \end{bmatrix}, \quad (A.5) \]
where \( R_\perp \) is the component of reflectivity perpendicular to the plane of incidence.

The rotation matrix, \([R]\), is utilized to transform a Mueller matrix in one coordinate system to its equivalent Mueller matrix in a rotated coordinate system and is given as \([33,41]\)
\[ [R(\phi)] = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos(2\phi) & \sin(2\phi) & 0 \\ 0 & -\sin(2\phi) & \cos(2\phi) & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad (A.6) \]
where \( \phi \) represents the angle of rotation about the axis of beam propagation in a direction counter-clockwise when looking into the direction of beam travel.

The rotation matrix can be used to transform a general Mueller matrix, \([M]\), in \(xyz\) coordinate system into its equivalent Mueller matrix, \([M']\), in the \(x'y'z\) coordinate system. The \(x'y'z\) is simply the \(xyz\) coordinate system rotated about the \(z\)-axis by an angle \( \phi \). The \([M']\) matrix is given as
\[ [M'] = [R(-\phi)][M][R(\phi)]. \quad (A.7) \]
Appendix B
Source Optics Angles

In Chapter 3, it was stated that the effects of the source optics could be described by the source matrix, \([L]\), as

\[
[L] = [R(-90°)][R(\gamma)][C_1][R(\beta)][P_1][R(\alpha)] , \tag{B.1}
\]

where \([R(\phi)]\) is the rotation matrix and the matrices \([C_1]\) and \([P_1]\) designate reflection from mirrors \(C_1\) and \(P_1\) (see Figure 3.1) at their respective angles of incidence (see Appendix A for the form of a reflection and rotation matrix).

Referring to Figure 3.1, the angles \(\alpha\), \(\beta\) and \(\gamma\) are defined as follows: (i) \(\alpha\) is the angle that \(\vec{n}_1\) must be rotated around axis \(LS-P_1\) to lie in the vertical plane, where \(\vec{n}_1\) is the vector normal to the \(LS-P_1-C_1\) plane, (ii) \(\beta\) is the angle that \(\vec{n}_1\) must be rotated around axis \(P_1-C_1\) to become parallel to \(\vec{n}_2\), where \(\vec{n}_2\) is the vector normal to the \(P_1-C_1-S\) plane and (iii) \(\gamma\) is the angle that \(\vec{n}_2\) must be rotated around axis \(C_1-S\) to lie in the vertical plane. Note that positive rotation is counter-clockwise when looking into the oncoming beam, as described in Chapter 2.
The angles $\alpha$, $\beta$, and $\gamma$ can be calculated by assigning cartesian coordinates to points $P_1$, $C_1$, and $S$ and then using the appropriate analytic geometry relations. As shown in Figure B.1, the cartesian coordinate system is chosen so that the origin is at $P_1$ and the $x$ and $z$ axes are both horizontal with the $z$ axis parallel to $LS-P_1$. Therefore, the $y$ axis is vertical with positive direction downward. The $(x, y, z)$ coordinates of point $C_1$ are denoted $(a, b, c)$ and are measured from the experimental apparatus. The position of point $S$ is defined as being at the same $x$ coordinate as point $C_1$ and the vector $\overrightarrow{C_1S}$ is at $45^\circ$ with respect to the $z$ axis. The positions of these points are summarized in Table B.1.

**Table B.1: Cartesian coordinates of the optical elements.**

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>$(x, y, z)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS</td>
<td>(0,0,-1)</td>
</tr>
<tr>
<td>$P_1$</td>
<td>(0,0,0)</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$(a, b, c)$</td>
</tr>
<tr>
<td>$S$</td>
<td>$(a, b + d, c + d)$</td>
</tr>
</tbody>
</table>

The first step is to find the normal vector to the $LS-P_1-C_1$ plane, $\vec{n}_1$. The equation describing a plane through any point $Q_1(x_1, y_1, z_1)$ and perpendicular to the direction $\{s, t, u\}$ is given as [103]

$$s(x - x_1) + t(y - y_1) + u(z - z_1) = 0 \quad \text{(B.2)}$$

Therefore, if the equation of a plane is known, the normal vector to that plane is
Figure B.1: Source optics geometry.
simply given as the coefficients of \( x, y \) and \( z \). The equation of a plane formed by the three points \( Q_1(x_1, y_1, z_1), Q_2(x_2, y_2, z_2) \) and \( Q_3(x_3, y_3, z_3) \) is given as [103]

\[
\begin{vmatrix}
x & y & z & 1 \\
x_1 & y_1 & z_1 & 1 \\
x_2 & y_2 & z_2 & 1 \\
x_3 & y_3 & z_3 & 1 \\
\end{vmatrix} = 0 , \tag{B.3}
\]

or, equivalently as

\[
\begin{vmatrix}
x - x_1 & y - y_1 & z - z_1 \\
x_2 - x_1 & y_2 - y_1 & z_2 - z_1 \\
x_3 - x_1 & y_3 - y_1 & z_3 - z_1 \\
\end{vmatrix} = 0 . \tag{B.4}
\]

Utilizing equation (B.4), the equation describing the LS-P\(_1\)-C\(_1\) plane is given as

\[-xb + ya = 0 , \tag{B.5}\]

where the points LS, P\(_1\) and C\(_1\) are defined in Table B.1. Comparing equations (B.2) and (B.5), it is seen that the normal vector to the LS-P\(_1\)-C\(_1\) plane is given as

\[\vec{n}_1 = \{-b, a, 0\} . \tag{B.6}\]

The angle \( \alpha \) is defined as the angle between \( \vec{n}_1 \) and the negative \( y \) axis, which is defined in terms of the dot product as

\[
\cos(\alpha) = \frac{\vec{n}_1 \cdot \hat{j}}{|\vec{n}_1| |\hat{j}|} = \frac{a}{\sqrt{b^2 + a^2}} , \tag{B.7}
\]

where \( \hat{j} \) is the unit vector parallel to the \( y \) axis, given as \( \{0, 1, 0\} \).

Again utilizing equation (B.4), the equation describing the P\(_1\)-C\(_1\)-S plane is given as

\[x(c - b) + ay - az = 0 , \tag{B.8}\]
where the points $P_1$, $C_1$ and $S$ are described in Table B.1. Comparing equations (B.2) and (B.8), it is seen that the normal vector to the $P_1$-$C_1$-$S$ plane is given as

$$\vec{n}_2 = \{c - b, a, -a\}.$$  

(B.9)

The angle $\beta$ is defined as the angle between $\vec{n}_1$ and $\vec{n}_2$ and is given in terms of the dot product as

$$\cos(\beta) = \frac{\vec{n}_1 \cdot \vec{n}_2}{|\vec{n}_1| |\vec{n}_2|} = \frac{a^2 + b^2 - bc}{\sqrt{(b - c)^2 + 2a^2} \sqrt{a^2 + b^2}}.$$  

(B.10)

As stated previously, $\gamma$ is the angle that $\vec{n}_2$ must be rotated around axis $C_1$-$S$ to lie in the vertical plane. Therefore, $\gamma$ is the angle between the vectors $\vec{n}_2$ and $\vec{m}$, where $\vec{m}$ is the vector in the $y-z$ plane (vertical plane) and perpendicular to the $C_1$-$S$ axis. With this definition, $\vec{m}$ is given as

$$\vec{m} = \{0, -1, 1\},$$  

(B.11)

and the angle $\gamma$ is given in terms of the dot product of $\vec{n}_2$ and $\vec{m}$ as

$$\cos(\gamma) = \frac{\vec{n}_2 \cdot \vec{m}}{|\vec{n}_2| |\vec{m}|} = \frac{-\sqrt{2} a}{\sqrt{(b - c)^2 + 2a^2}}.$$  

(B.12)

Referring to Figure B.1, the angle of incidence on mirror $P_1$, $\phi_1$, is given as half of the angle between the incident beam, vector $\vec{P}_1 - \vec{L} S$, and the reflected beam, vector $\vec{P}_1 - \vec{C}_1$. The vectors $\vec{P}_1 - \vec{L} S$ and $\vec{P}_1 - \vec{C}_1$ are given as $\{0, 0, -1\}$ and $\{a, b, c\}$, respectively. With this definition of the incident and reflected beam directions, the angle of incidence on mirror $P_1$ is given as

$$\cos(2\phi_1) = \frac{\vec{P}_1 - \vec{L} S \cdot \vec{P}_1 - \vec{C}_1}{|\vec{P}_1 - \vec{L} S| |\vec{P}_1 - \vec{C}_1|} = \frac{\{0, 0, -1\} \cdot \{a, b, c\}}{|\{0, 0, -1\}| |\{a, b, c\}|}$$
Similarly, the angle of incidence on mirror \( C_1 \), \( \phi_2 \), is given as half of the angle between the incident beam, vector \( \overrightarrow{C_1-P_1} \), and the reflected beam, vector \( \overrightarrow{C_1-S} \), where the vectors \( \overrightarrow{C_1-P_1} \) and \( \overrightarrow{C_1-S} \) are given as \( \{-a, -b, -c\} \) and \( \{0,1,1\} \), respectively. Therefore, the angle of incidence on mirror \( C_1 \) is given as

\[
\cos(2\phi_2) = \frac{\overrightarrow{C_1-P_1} \cdot \overrightarrow{C_1-S}}{|\overrightarrow{C_1-P_1}||\overrightarrow{C_1-S}|} = \frac{\{-a, -b, -c\} \cdot \{0,1,1\}}{|\{-a, -b, -c\}| |\{0,1,1\}|}
\]

\[
= \frac{-(b + c)}{\sqrt{2} \sqrt{a^2 + b^2 + c^2}} .
\]

Now that all angles are defined in terms of the distances \( a \), \( b \) and \( c \), a simple measurement of these distances will define the angles of interest. The measured distances and the inferred angles are shown in Table B.2.

Table B.2: Source optics distances and angles.

<table>
<thead>
<tr>
<th>Distance</th>
<th>Inches</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>-5.75</td>
</tr>
<tr>
<td>( b )</td>
<td>-1.6</td>
</tr>
<tr>
<td>( c )</td>
<td>-3.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angle</th>
<th>Degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>15.6</td>
</tr>
<tr>
<td>( \beta )</td>
<td>53.3</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>13.8</td>
</tr>
<tr>
<td>( \phi_1 )</td>
<td>29.5</td>
</tr>
<tr>
<td>( \phi_2 )</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Appendix C

General Optical System

It was stated in Section 3.4.2 that the intensity of unpolarized light transmitted through a general optical system positioned between a polarizer and analyzer is a sinusoidal function with respect to the polarizer ($P$) and analyzer ($A$) azimuths. This appendix will utilize the Mueller calculus to prove this result.

The overall Mueller matrix, $[M]$, of a general optical system positioned between a polarizer and analyzer is given as

$$[M] = [A][T][P] \quad (C.1)$$

where $[P]$ and $[A]$ represent the Mueller matrices of the polarizer and analyzer, respectively, and $[T]$ represents the Mueller matrix of a completely general optical system. For an unpolarized incident beam, the intensity of light transmitted by this optical system is given as the $(1,1)$ element (see Section 2.3) of the Mueller matrix, $[M]_{1,1}$. Utilizing the Mueller matrix for a polarizing element shown in Appendix A, the $(1,1)$ element of matrix $[M]$ in equation (C.1) is given as
\[ [M]_{1,1} = t_{1,1} + t_{1,2} \cos(2P) + t_{1,3} \sin(2P) \]
\[ + \cos(2A) [t_{2,1} + t_{2,2} \cos(2P) + t_{2,3} \sin(2P)] \]
\[ + \sin(2A) [t_{3,1} + t_{3,2} \cos(2P) + t_{3,3} \sin(2P)] \quad , \quad \text{(C.2)} \]

where \( t_{i,j} \) are the elements of matrix \([T]\). It is seen in equation (C.2) that if \( A \) is held constant, \([M]_{1,1} \) is a sinusoidal function with respect to \( P \), with a period of 180 degrees. Similarly, if \( P \) is held constant, \([M]_{1,1} \) is a sinusoidal function with respect to \( A \), with a period of 180 degrees.
Appendix D

Experimental Data Sheets

This appendix includes a representative data sheet for each of the sample materials considered, which are amorphous carbon, pyrolytic graphite and flame soot. Each data sheet contains information about selected optical components and equipment settings, as well as the intensity measurements.
Date: 8-28-91

Sample: Amorphous Carbon

Wavelength: 500 nm

Iris Openings: 1st: 1/8 in. 2nd: 1/8 in.

Source: Xe Lamp

Detector: RCA 1P28A PMT

Detector Voltage: 540 V

Polarizers: #27340

Filter: 0.4 μm LWP

Slit Openings: 0.4 mm

Lock-in-Amp Time Constant: 3 sec.

Furnace Temp.: 600°C

Corrections for Polarizer and Analyzer:

δA = 3.0°  δP = -4.7°

Analyzer Scale Reading = A₀ = 325°

A = (360° − A₀) + δA = 38°

Inert Gas: Helium

Windows: Both

Table D.1: Experimental ellipsometry data from amorphous carbon.

<table>
<thead>
<tr>
<th>P₀</th>
<th>Intensity (mV)</th>
<th>P₀</th>
<th>Intensity (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>438.9</td>
<td>180</td>
<td>429.9</td>
</tr>
<tr>
<td>20</td>
<td>135.8</td>
<td>200</td>
<td>132.1</td>
</tr>
<tr>
<td>40</td>
<td>25.06</td>
<td>220</td>
<td>25.40</td>
</tr>
<tr>
<td>60</td>
<td>152.1</td>
<td>240</td>
<td>161.9</td>
</tr>
<tr>
<td>80</td>
<td>460.6</td>
<td>260</td>
<td>478.2</td>
</tr>
<tr>
<td>100</td>
<td>807.8</td>
<td>280</td>
<td>815.6</td>
</tr>
<tr>
<td>120</td>
<td>1027.9</td>
<td>300</td>
<td>1019.7</td>
</tr>
<tr>
<td>140</td>
<td>1007.6</td>
<td>320</td>
<td>1005.3</td>
</tr>
<tr>
<td>160</td>
<td>779.1</td>
<td>340</td>
<td>774.6</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>360</td>
<td>439.0</td>
</tr>
</tbody>
</table>
Date: 8-30-91

Sample: Pyrolytic Graphite

Time: 4:30 p.m.

Wavelength: 500 nm  

File: [.PG2K]PG500D.DAT

Iris Openings: 1st: 1/8 in.  

2nd: 1/8 in.  

Slit Openings: 0.4 mm

Source: Xe Lamp  

Detector: RCA 1P28A PMT

Detector Voltage: 524 V

Polarizers: #27340  

Filter: 0.4 μm LWP

Lock-in-Amp Time Constant: 3 sec.  

Furnace Temp.: 600°C

Corrections for Polarizer and Analyzer:

δA = 3.0°  

δP = -4.7°

Analyzer Scale Reading = A₀ = 325°

A = (360° − A₀) + δA = 38°

Windows: Both  

Inert Gas: Helium

Table D.2: Experimental ellipsometry data from pyrolytic graphite sample.

<table>
<thead>
<tr>
<th>PS</th>
<th>Intensity (mV)</th>
<th>PS</th>
<th>Intensity (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>381.7</td>
<td>180</td>
<td>378.1</td>
</tr>
<tr>
<td>20</td>
<td>137.0</td>
<td>200</td>
<td>133.5</td>
</tr>
<tr>
<td>40</td>
<td>24.03</td>
<td>220</td>
<td>23.60</td>
</tr>
<tr>
<td>60</td>
<td>94.3</td>
<td>240</td>
<td>100.1</td>
</tr>
<tr>
<td>80</td>
<td>315.8</td>
<td>260</td>
<td>325.7</td>
</tr>
<tr>
<td>100</td>
<td>589.4</td>
<td>280</td>
<td>595.6</td>
</tr>
<tr>
<td>120</td>
<td>777.6</td>
<td>300</td>
<td>776.5</td>
</tr>
<tr>
<td>140</td>
<td>796.9</td>
<td>320</td>
<td>792.9</td>
</tr>
<tr>
<td>160</td>
<td>640.7</td>
<td>340</td>
<td>639.3</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>360</td>
<td>382.9</td>
</tr>
</tbody>
</table>
Date: 9-26-91

Sample: Soot Pellet

Wavelength: 500 nm
Iris Openings: 1ˢᵗ: 1/8 in. 2ⁿᵈ: 1/8 in.

Source: Xe Lamp
Detector: RCA 1P28A PMT
Detector Voltage: 625 V

Polarizers: #27340
Filter: 0.4 μm LWP

Lock-in-Amp Time Constant: 3 sec.    Furnace Temp.: 600°C

Corrections for Polarizer and Analyzer:
δA = 2.8°      δP = -4.7°

Analyzer Scale Reading = \(A_v = 325°\)

\(A = (360° - A_v) + δA = 37.8°\)

Windows: Both    Inert Gas: Helium

Table D.3: Experimental ellipsometry data from soot pellet.

<table>
<thead>
<tr>
<th>Pₛ</th>
<th>Intensity (mV)</th>
<th>Pₛ</th>
<th>Intensity (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>171.6</td>
<td>180</td>
<td>167.8</td>
</tr>
<tr>
<td>20</td>
<td>37.46</td>
<td>200</td>
<td>36.24</td>
</tr>
<tr>
<td>40</td>
<td>75.44</td>
<td>220</td>
<td>78.85</td>
</tr>
<tr>
<td>60</td>
<td>268.8</td>
<td>240</td>
<td>276.5</td>
</tr>
<tr>
<td>80</td>
<td>532.8</td>
<td>260</td>
<td>538.8</td>
</tr>
<tr>
<td>100</td>
<td>736.0</td>
<td>280</td>
<td>737.0</td>
</tr>
<tr>
<td>120</td>
<td>783.1</td>
<td>300</td>
<td>778.0</td>
</tr>
<tr>
<td>140</td>
<td>657.1</td>
<td>320</td>
<td>651.6</td>
</tr>
<tr>
<td>160</td>
<td>416.4</td>
<td>340</td>
<td>412.3</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>360</td>
<td>170.4</td>
</tr>
</tbody>
</table>
Date: 8–23–91

Time: 11:30 a.m.

Sample: Silicon Wafer

Wavelength: 633 nm

File: [.SIIC]SI633A.DAT

Iris Openings: 1st: 1/8 in. 2nd: 1/8 in. Slit Openings: 0.4 mm

Source: Xe Lamp

Detector: RCA 1P28A PMT

Detector Voltage: 655 V

Polarizers: #27340

Filter: 0.4 μm LWP

Lock-in-Amp Time Constant: 3 sec. Furnace Temp.: 25°C

Corrections for Polarizer and Analyzer:

δA = 3.0°  δP = −4.7°

Analyzer Scale Reading = Av = 325°

A = (360° − Av) + δA = 38°

Windows: Both Inert Gas: Helium

Table D.4: Experimental ellipsometry data from silicon wafer.

<table>
<thead>
<tr>
<th>PS</th>
<th>Intensity (mV)</th>
<th>PS</th>
<th>Intensity (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>472.1</td>
<td>180</td>
<td>460.2</td>
</tr>
<tr>
<td>20</td>
<td>172.8</td>
<td>200</td>
<td>166.1</td>
</tr>
<tr>
<td>40</td>
<td>14.94</td>
<td>220</td>
<td>13.43</td>
</tr>
<tr>
<td>60</td>
<td>67.50</td>
<td>240</td>
<td>74.66</td>
</tr>
<tr>
<td>80</td>
<td>301.0</td>
<td>260</td>
<td>321.1</td>
</tr>
<tr>
<td>100</td>
<td>619.3</td>
<td>280</td>
<td>622.6</td>
</tr>
<tr>
<td>120</td>
<td>867.9</td>
<td>300</td>
<td>844.1</td>
</tr>
<tr>
<td>140</td>
<td>905.6</td>
<td>320</td>
<td>915.1</td>
</tr>
<tr>
<td>160</td>
<td>757.8</td>
<td>340</td>
<td>754.7</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>360</td>
<td>473.1</td>
</tr>
</tbody>
</table>
Appendix E

Computer Programs

This appendix contains a list of the FORTRAN computer programs utilized throughout the course of this work. Each entry contains the name of the program along with a brief description of its function. A complete listing of each of these programs is on file with the Lasers and Combustion Diagnostics Laboratory at LSU.

DIRECTORY: [ MECHAR1.BARRY.PROGSFOR.ELPINV ]

1. CLMOS.FOR: Evaluate the density from the Clausius–Mossotti equation.

2. CLMOS3.FOR: Evaluate refractive index \((n, k)\) from Clausius–Mossotti equation.

3. DISPCON.FOR: Evaluate the Drude–Lorentz dispersion parameters from experimentally determined values of refractive index.

4. ELPDFT.FOR: Reduce a single set of ellipsometry data to evaluate the ellipsometric parameters and the refractive index of a sample.
5. ELPDFTM.FOR: Reduce multiple sets of ellipsometry data at one time to evaluate the ellipsometric parameters and the refractive index of a sample.

6. FNDPOL.FOR: Solve for the reference positions of the polarizer and analyzer based on three experimental measurements.

7. WINDFT1.FOR: Calculate the birefringence parameters of the entrance window from ellipsometry intensity data, assuming that the sample properties are known.

8. WINDFT2.FOR: Calculate the birefringence parameters of the exit window from two sets of ellipsometry intensity data, assuming that the sample properties are known.

DIRECTORY: [MECHAR1.BARRY.PROGSFOR.ELLIPSE]

1. ERRNK.FOR: Calculate the error in refractive index due to error in intensity readings.

2. FOURSNS.FOR: Plot a grid of lines of constant refractive index versus the two measured Fourier coefficients.

3. L1L2.FOR: Calculate the source optics parameters versus wavelength.

4. OPTFOUR.FOR: Calculate the optimum angle of incidence and optimum analyzer azimuth as functions of the refractive index.
5. POLLEAK.FOR: Calculate the effects of polarizer leakage on ellipsometry measurements.
Vita

Barry James Stagg was born in Eunice, Louisiana on January 14, 1964 to parents Roy and Juanell Stagg. He received his B.S. degree in Mechanical Engineering from Louisiana State University in 1986, where he graduated cum laude and was named Outstanding Senior in Mechanical Engineering for that year. In 1992, he received his Ph.D. in Mechanical Engineering from the same university. He has co-authored five technical publications in the areas of combustion and optical diagnostics and they are listed below.


DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Barry James Stagg

Major Field: Mechanical Engineering

Title of Dissertation: Development of a Technique to Determine the Temperature Dependence of the Refractive Index of Carbonaceous Particulates

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Dr. D. Temple

Dr. V. Cundy

Dr. T. Myrum

Dr. M. Sabbaghian

Dr. N. Kestner

Date of Examination: 3/31/92