ABSTRACT

ASAR, MUHARREM. Anisotropy Effects In Real-Time Optical Diagnostics Of Epitaxial Growth And Associated Metrology Instrumentation (Under the direction of Professor David E. Aspnes)

As new applications in metrology force the evolution of accuracies from the 1-2% range characteristic of rotating-polarizer and rotating-analyzer ellipsometers to 0.1-0.2%, ellipsometric technology is rapidly moving to rotating-compensator designs. In addition, new classes of artifacts become relevant. This work is a thorough investigation of various effects related to optically anisotropic components and samples, including the monoplate compensator, the effect of axial misalignments on the accuracy of ellipsometric measurements, and the effect of sample anisotropy on ellipsometric data obtained during real-time measurements of epitaxial growth.

Advances include generalization of the Jones-matrix formulism to 3 dimensions to describe axially misaligned components, an improvement of the widely used formulation of Yeh that eliminates singularities in the calculation of transmittance and reflectance properties of anisotropic materials, and a Taylor-series approach to calculate the effect of thin anisotropic surface layers on complex reflectances thereby avoiding the need to diagonalize matrices. I provide the first analysis of the monoplate compensator, a next-generation device for broadband spectroscopic ellipsometry, showing that the even Fourier coefficients in the transmitted intensity in instruments using this device provide information about the sample and odd coefficients about system alignment, with the even coefficients affected only to second order in misalignment parameters. Alignment procedures are developed, and misalignments that create other types of artifacts in the determination of surface anisotropies in rotating-sample OMCVD reactors that are analyzed and discussed.

In general, the work provides new insight into the treatment of the properties of optically anisotropic materials in both data analysis and metrology instrumentation, and allows for increased accuracy in the analysis of ellipsometric data.
ANISOTROPY EFFECTS IN REAL-TIME OPTICAL DIAGNOSTICS OF EPITAXIAL GROWTH AND ASSOCIATED METROLOGY INSTRUMENTATION

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To my family
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Chapter 1

1 INTRODUCTION

Advances in semiconductor technology are resulting in continuing decreases in the sizes of device features and the introduction of new materials into fields traditionally dominated by Si and a few III-V compound semiconductors. These trends have shown no signs of slowing down in recent years, and in fact appear to be coming at an increasingly rapid rate. These changes are bringing new challenges to metrology, which is defined as the science of measurement.

While a number of approaches involving both optical and particle (electron and ion) spectroscopies are in general use in semiconductor technology, optical diagnostics are becoming increasingly important owing to their nondestructive nature and their capability of being used in any transparent ambient. Of these, spectroscopic ellipsometry (SE) is becoming increasingly attractive owing to its ability to measure properties of layers whose thicknesses are well into the sub-Angstrom range. Examples of applications here include real-time assessment and control of epitaxial growth. More recently, SE has been applied to the determination of the characteristics of patterned samples (the so-called RT/CD or real-time critical dimensions problem.) In this application SE data are analyzed for cross-sectional information on patterned materials, for example widths of features in photoresists and the determination of undercutting artifacts, sidewall angles, and general structural
characteristics in etched materials. RT/CD applications are particularly intriguing since the result is that SE is now making inroads into applications previously done exclusively by scanning electron microscopy (SEM). [1]

These new challenges have had a major impact on SE technology as well. In particular, the RT/CD applications require SE to achieve accuracies of 0.1-0.2% instead of the 1-2% characteristic of the rotating-polarizer (RPE) and rotating-analyzer (RAE) ellipsometer configurations that have dominated SE technology for the last 30 years. As a result SE instrumentation is rapidly moving toward phase-modulated configurations, which provide more diagnostic power and eliminate certain classes of artifacts characteristic of rotating-polarizer designs. In phase-modulated systems the azimuth angles of the polarizer and analyzer prisms are fixed, and the time dependence needed to analyze sample properties is generated through the use of photoelastic modulators or rotating compensators (retarders, waveplates). However, since photoelastic modulators operate at too high a frequency for use with photodiode-array or CCD detectors, attention is currently being focused on rotating-compensator ellipsometer (RCE) designs. These replace the rotating prism with a rotating compensator of either biplate, Berek, or monoplate design.

In the area of real-time diagnostics of epitaxial growth, decreasing device sizes increase the need to understand and control the growth of compound semiconductors on the Angstrom scale. At this level the determination of surface processes becomes even more critical, since these establish growth mechanisms. Optical diagnostics are making additional contributions here through the measurement of the optical anisotropies of surfaces, which are directly related to surfaced chemistry and hence the growth processes themselves. In fact with organometallic chemical vapor deposition (OMCVD), which is done at relatively high pressures, optical diagnostics are the only method of obtaining information about growth surfaces. Since the additional dimension of chemistry is rapidly making OMCVD an industry standard for epitaxial deposition, the development of rapid, accurate optical techniques for assessing OMCVD growth is also becoming increasingly important. This need is currently being met by reflectance-difference (-anisotropy) spectroscopy (RDS/RAS),
where the sample anisotropy is measured directly and in cubic materials where the bulk is optically isotropic, originates entirely from the growth surface. Ideally, the measurement of ellipsometric and surface-anisotropy properties should be combined in a single-beam system that will return both types of information at once. A difficulty here is that anisotropy data are typically of the same order as instrumentation noise levels and hence more affected than the ellipsometric data by system artifacts and noise.

As a result of these recent advances SE technology has advanced faster than our understanding of it. In particular, the need to achieve an order of magnitude increase in accuracy requires the analysis of new classes of artifacts, for example those due to depolarization effects in samples and multiple scattering in components. In addition, we need a better understanding of the components themselves. One area that has received essentially no attention is axial misalignment. The standard procedure of analyzing optical systems is to use Jones matrices, but these (2x2) matrices assume that the components themselves are axially aligned. In particular, the recently invented monoplate compensator has received essentially no attention, even though this component has a unique potential for metrology since it provides considerably more information about system artifacts while eliminating a number of the problems associated with the more common biplate and Berek compensators.

Consequently, there is a major current need to extend our capabilities of properly modeling optical instrumentation. Assumptions of ideal behavior in device modeling do not meet the needs for high accuracies and hence more representative solutions are required. In particular, RCE configurations provide considerably more information about the sample than possible with RAE and RPE designs, but they also provide more information about system artifacts and hence are considerably more difficult to analyze. Meeting these needs is the objective of this work. I consider each element of SE separately, addressing the problem of axial misalignment by using an extended (3x3) Jones-matrix formulation to take into account the effects of the third dimension. The monoplate is analyzed thoroughly, showing that in contrast to the other two types of compensators it provides useful information about system
alignment in general and beam alignment in particular. The effect of these artifacts on sample information is considered. The work resolves a major need in that it provides a systematic treatment of these effects, which has not been done before. In addition, I show that the previous standard work of Yeh is incomplete in that it yields singularities in solutions for the normal-mode vectors of optically uniaxial materials. I show that these singularities can be avoided by appropriate procedures developed here.

Finally, I consider in detail the determination of surface optical anisotropies in the integrated RD/SE spectrometer developed in this laboratory for monitoring and controlling epitaxial growth by OMCVD. Anisotropy spectra obtained at non-normal incidence, here at an angle of 71°, are related to the normal-incidence anisotropy spectra commonly reported in the literature. I show that at non-normal incidence it is also possible to distinguish bulk and surface contributions. The work concludes by applying these results to the analysis of homo- and heteroepitaxial growth of GaSb in our OMCVD reactor.
This chapter is intended to give a brief background of electromagnetic theory of propagation. Optical properties of semiconductors and interfaces, and applications to optical components with its methods will be given after the theory is established. Theory and application of optical diagnostics tools used ex-situ and in-situ (integrated with OMCVD reactor), i.e., ellipsometry and RDS will also be discussed. Basic anisotropy information from the literature will also be given.

2.1 Maxwell Equations and Dielectric Function

In electrodynamics, the measurable quantities are fields, specifically the macroscopic averages of microscopic fields over microscopically large areas. The starting point, which is where the basic physics takes place, is at the atomic scale.

Maxwell's equations in microscopic form (SI units) are

\[ \nabla \cdot \mathbf{B} = 0, \quad (2.1) \]

\[ \nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \quad (2.2) \]
\[\nabla \cdot E = \frac{\rho}{\varepsilon_0}, \quad (2.3)\]

\[\nabla \times B - \frac{1}{c^2} \frac{\partial E}{\partial t} = \mu_0 J. \quad (2.4)\]

For our purposes we will be dealing with macroscopic averages, so we can perform spatial and temporal averages of Eqs.(2.1)-(2.4) to get the corresponding macroscopic forms. Two of these equations have exactly the same form:

\[\nabla \cdot \langle B \rangle = 0, \quad (2.5)\]

\[\nabla \times \langle E \rangle + \frac{\partial \langle B \rangle}{\partial t} = 0. \quad (2.6)\]

whereas the other two require some work. The brackets \(\langle \rangle\) in the above represent averaging over both space and time. To write Eqs.(2.3) and (2.4) in macroscopic form we need to consider charges and current density in more detail. Free charges are electrons in the conduction band and holes in the valence band. Bound charges are charges confined within the material, for example charges in valence bonds or intrinsic molecular dipoles or induced dipoles. An applied external field acts to align existing dipoles in its direction. In the limit that the dipole density is uniform the effective charge density vanishes. If the dipole density is not uniform (Figure 2-1), then there is a net bound charge density. Therefore Eq.(2.3) can be written as

\[\nabla \cdot \langle E \rangle - \frac{\langle \rho_b \rangle}{\varepsilon_0} = \frac{\langle \rho_f \rangle}{\varepsilon_0}. \quad (2.7)\]

For the case of bound charges, the applied field causes a change in charge density as a result of the forces exerted on the individual charges. We can represent this field-induced change by defining an electric dipole as charge times displacement, then averaging the
resulting dipoles over the volume of the material to get the dipole moment per unit volume, or dipole density. This can be written

\[
\langle \mathbf{p} \rangle = \frac{1}{V} \int \rho_b r_i d^3 \mathbf{r} = \frac{1}{V} \sum_i^N q_i \Delta r_i .
\] (2.8)

Integrating the above equation by parts, we can represent the field-induced change in the charge density as

\[
\rho_b = -\nabla \cdot \langle \mathbf{P} \rangle .
\] (2.9)

Note that the induced charge density has a sign opposite to that of the applied field. We drop the bracket notation for convenience and substitute this into the Eq. (2.7). Combining the divergence terms we obtain the macroscopic form of Eq. (2.3)

\[
\nabla \cdot \mathbf{D} = \rho_f .
\] (2.10)

The same procedure with somewhat different physics applies to the current density. The difference is due in principle to pre-existing magnetic dipoles, which can line up and contribute to the total field under the action of a macroscopic current density for example. The relevant equation is

\[
\nabla \times \mathbf{B} - \mu_0 \mathbf{j}_b - \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} = \mu_0 \mathbf{j}_f .
\] (2.11)

By writing \( \mathbf{j}_b \) as

\[
\mathbf{j}_b = \frac{\partial \mathbf{P}}{\partial t} + \nabla \times \mathbf{M} ,
\] (2.12)

and substituting this into Eq. (2.11) we get the macroscopic form of Eq. (2.4):
\[ \nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{J}_f, \quad (2.13) \]

where \( \mathbf{D} \) is called the displacement vector and \( \mathbf{H} \) is called magnetic field. The relationship between these quantities is

\[ \mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M}, \quad (2.14) \]

\[ \mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}, \quad (2.15) \]

\[ \mathbf{P} = \varepsilon_0 \chi \mathbf{E}, \quad (2.16) \]

\[ \varepsilon = \varepsilon_0 (1 + \chi). \quad (2.17) \]

where \( \varepsilon \) is the dielectric tensor and \( \chi \) the electric susceptibility.

![Figure 2-1 Molecular dipoles with non-uniform polarization.](image)

Equations (2.16) and (2.17) define the dielectric function. If the polarization is always parallel to applied electric field for a given material, then \( \chi \) and therefore \( \varepsilon \) are
scalar. This is the case for media with cubic or spherical symmetry. However, there is no priori reason that the polarization should always be in the direction of the applied field. This is the case for optically anisotropic materials, for which the electric susceptibility and therefore the dielectric function are second rank tensors. This topic is fundamental to the work discussed here and will be treated in later sections.

2.2 Dielectric Response, Scalar Systems

Simple Force Model for the Dielectric Tensor

In the previous section we described and defined dielectric tensor in terms of dipole moments. These dipoles can also be seen as negative bound charges around positive nuclei and therefore under an applied field disturbance occurs and dipoles form. As a result the dielectric response of the material depends on the energy and the intensity of the field applied to it. Intensity mostly effects the higher order terms in dielectric susceptibility $\chi$ (non-linear optics). For linear region we are interested the frequency dependence of a dielectric response of a material.

For a simple model we can consider a charge under the action of an applied electric field. We can neglect the magnetic field contribution because $v \ll c$. We include a linear restoring force (Hooke’s Law) and frictional losses. Then the equation of motion can be written

$$F = ma = qE - K(r - r_0) - bv.$$  

(2.18)

Assuming an $e^{-i\omega t}$ dependence on the field and displacement vectors

$$E = E_0 e^{-i\omega t},$$  

(2.19)

$$r = r_0 + \Delta r e^{-i\omega t}.$$  

(2.20)

Therefore Eq. (2.18) can be rewritten as
\[ F = -m\omega^2 \Delta r e^{-i\alpha t} = qE_0 e^{-i\omega t} - K\Delta r e^{-i\alpha t} + i\omega b \Delta r e^{-i\alpha t}. \] (2.21)

The solution of Eq.(2.21) is

\[ \Delta r = \frac{qE_0}{K - m\omega^2 - i\omega b}. \] (2.22)

Using Eqs.(2.8) and (2.17), the dielectric function of frequency becomes

\[ P = \frac{Nq^2 E_0}{V(K - m\omega^2 - i\omega b)}, \] (2.23)

\[ \frac{\varepsilon}{\varepsilon_0} = 1 + \frac{nq^2}{(K - m\omega^2 - i\omega b)}, \] (2.24)

where \( n = \frac{N}{V} \).

Assuming that charges might behave differently with different strengths and losses, more terms may be added in Eq.(2.24). This will be seen as the particular structure of a material in a typical dielectric function spectra as a function of energy. Rearranging terms and considering multiple oscillators Eq.(2.24) can be written as the spectral representation [2]

\[ \frac{\varepsilon}{\varepsilon_0} = 1 + \sum_j \frac{\omega^2}{(\omega^2_j - \omega^2 - i\omega_0 \gamma_j)} \] (2.25)

where \( \omega_p = \sqrt{nq^2/m} \), \( \omega_0 = \sqrt{K/m} \), \( \gamma = b/m \).

The above equation is a general spectral representation of a dielectric function. It satisfies the linearity, causality and reality conditions.
\[
\frac{\varepsilon}{\varepsilon_0} = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2 - i\omega\gamma)} = 1 - \frac{\omega_p^2 (\omega^2 - \omega_0^2)}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2} + i \frac{\omega_p^2 \omega \gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2}.
\] (2.26)

For \( \omega = \omega_0 \) and \( \gamma \ll \omega_0 \) the lineshape is Lorentzian and Eq.(2.26) can be written as

\[
\frac{\varepsilon}{\varepsilon_0} = 1 - \frac{\omega_p^2 (\omega - \omega_0)}{2\omega_0 [ (\omega - \omega_0)^2 + \Gamma^2]} + i \frac{\omega_p^2 \Gamma}{2\omega_0 [ (\omega - \omega_0)^2 + \Gamma^2]},
\] (2.27)

where \( \Gamma = \frac{\gamma}{2} \).

As seen from Eq.(2.27) the dielectric function is a complex quantity. Hence it can be divided into its real and imaginary parts as

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2. \] (2.28)

Figure 2-2 shows the real and imaginary parts of the dielectric function of Si along with a least-squares fit using four Lorentz oscillators, one each for the three individual peaks and one as a general broad peak underlying these three. Although the representation describes the main features, as seen in the figure, this approach is not practical for data analysis because it involves too many parameters (3 for each Lorentzian oscillator) and does not represent the data to the level of accuracy needed for actual applications.
2.3 Boundary Conditions

Since all semiconductor devices of practical importance are layered, optical data obtained on layered structures during growth must be accurate and modeled carefully so that the resulting analyses are also accurate. As the feature size of semiconductor components becomes smaller and the thickness of grown layers approaches the angstrom scale, real-time diagnostics must be able to detect changes that occur on time scales of the order of the time required to deposit one monolayer. Therefore we need to give particular attention to semiconductor interfaces.

The basic descriptor of the optical properties of laminar systems in the n-layer model, where (n−2) is the number of layers present (the first and last indices are reserved for substrate and ambient, respectively.) Before discussing the n-layer model in detail, I review
the boundary conditions that the fields must satisfy. Solving the Maxwell equations for a
given material yields the \( E \) and \( H \) fields within the layer, and these solutions need to be
connected. The connection is done via the boundary conditions. At the interface these
conditions are \([3]\)

\( i) \) The normal component of displacement vector along the interface is discontinuous
if an interface charge density is present and continuous otherwise:

\[
(D_1 - D_2) \cdot \hat{n} = \sigma_f .
\]  

\( ii) \) The tangential component of electric field parallel to the interface is continuous:

\[
(E_1 - E_2) \times \hat{n} = 0 .
\]  

\( iii) \) The normal component of the magnetic induction is continuous:

\[
(B_1 - B_2) \cdot \hat{n} = 0 .
\]  

\( iv) \) The tangential component of the magnetic field parallel to the interface is
discontinuous if a surface current is present and continuous otherwise:

\[
(H_1 - H_2) \cdot \hat{n} = J_f .
\]  

In a medium where there are no free charges or free currents present, our solutions
will be plane waves. Combining the Maxwell equations we first obtain the Helmholtz wave
equation followed by the dispersion equation when the plane-wave solution are substituted.
These are

\[ \nabla^2 E - \nabla (\nabla \cdot E) + \frac{\omega^2 \mu \epsilon}{c^2} E = 0 , \]  

\( 2.33 \)
\[ \mathbf{k} (\mathbf{k} \cdot \mathbf{E}) - k^2 \mathbf{E} + \frac{\omega^2 \mu \epsilon}{c^2} \mathbf{E} = 0. \]  \hspace{1cm} (2.34)

Solution of Eq. (2.34) together with the use of the boundary conditions between layers allows the reflection and transmission coefficients to be calculated. Hence given an incident plane-wave state of a given polarization and propagation direction, the polarization and direction of the reflected wave can be determined. Note for the crystal-optics applications of interest here the first term in Eq. (2.34) is crucial, even though it is not usually in the Helmholtz equation.

Equation (2.34) is actually three equations, one for each Cartesian direction, and its solution in general involves the inversion of a $3 \times 3$ matrix called the dispersion matrix. For an isotropic material the $3 \times 3$ dispersion matrix becomes trivial, yielding a degenerate double root that is a quadratic equation for the propagation vector. The analytic solution is easy to obtain. However if the layer is anisotropic, either a quadratic or quartic equation will be obtained. In many cases analytical representations are impractical and numerical analysis is needed, although where possible we consider a middle ground, deriving analytic expressions for first-order effects. Details are given in later sections.

### 2.4 Model Calculations

#### 2.4.1 Two Layer Model

The geometry of the two-phase (substrate/ambient) model is shown in Figure 2-3. Polarizations parallel (TM) and perpendicular (TE) to the plane of incident are denoted as $p$ and $s$ respectively. The complex reflection coefficients for $p$- and $s$-polarized waves can be derived from the Fresnel equations and are given as

\[ r_p = \frac{\epsilon_p n_{p \perp} - \epsilon_s n_{s \perp}}{\epsilon_p n_{p \perp} + \epsilon_s n_{s \perp}}, \]  \hspace{1cm} (2.35)

\[ r_s = \frac{n_{p \perp} - n_{s \perp}}{n_{p \perp} + n_{s \perp}}, \]  \hspace{1cm} (2.36)
where \( n_{j\perp} = \sqrt{\varepsilon_j - \varepsilon_a \sin^2 \theta} \), \( j = a, s \) and \( \theta \) is angle of incidence. These equations can be inverted to give the dielectric function of the substrate:

\[
\frac{\varepsilon_j}{\varepsilon_a} = \sin^2 \theta \left( 1 + \tan^2 \theta \left( \frac{1 - \rho}{1 + \rho} \right)^2 \right),
\]

(2.37)

where \( \rho \) is the complex reflection coefficient ratio defined as

\[
\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta},
\]

(2.38)

Figure 2-3 Geometry of the two-phase model, which consists of a uniform substrate and transparent ambient. Incident and reflected electric fields are also shown. \( p \) and \( s \) indicates polarization parallel and perpendicular to the plane of incidence, respectively.

Equations (2.35) and (2.36) are also used for multilayer models since they also describe the impedance mismatch between adjacent layers. More generally, if the uppermost layer is optically thick, then the multilayer model reduces to the two-layer model. For arbitrary multilayer models we can still substitute the measured value of \( \rho \) into Eq.(2.37),
since it basically describes a change of variables. The result is called a pseudodielectric function. This is another representation of the complex reflectance ratio $\rho$ [4] and can also be used to extract thickness and overlayer information by means of an appropriate model.

### 2.4.2 Three Layer Model

The three-layer model, another special case of the n-layer model, consists of a substrate, an overlayer and the ambient as shown in Figure 2-4. It is the most widely used model for epitaxial growth. Models that have more than three layers can be reduced to three-layer model by making the common pseudosubstrate approximation [4], which assumes that all material beneath the topmost layer can be treated as a pseudosubstrate. Although this is an approximation, for the semiconductor materials of interest for the integrated OMCVD/optical diagnostics system [5], this approximation is more accurate than the data. In particular, it allows us to extract the dielectric function of the depositing overlayer at rates of several spectra per monolayer. The pseudosubstrate approximation is also very useful for extracting overlayer information for very thin layers.

![Three phase model](image)

**Figure 2-4** Three phase model consisting of a substrate, and overlayer, and the ambient, showing incident and reflected fields.

The reflection coefficients for the three-layer model are
\[ r_{p,oa} = \frac{r_{p,oa} + r_{p,so}Z}{1 + r_{p,oa}r_{p,so}Z}, \]  
(2.39)

\[ r_{s,oa} = \frac{r_{s,oa} + r_{s,so}Z}{1 + r_{s,oa}r_{s,so}Z}, \]  
(2.40)

where \( r_{oa} \) and \( r_{so} \) are the reflection coefficients for p- and s-polarized waves of a two-layer model and \( Z \) is the back-reflection phase term defined as

\[ Z = \exp\left(4\pi n_{o,\perp}d/\lambda\right). \]  
(2.41)

Unlike the case of the two-layer model, Eqs.(2.39) and (2.40) do not have an analytical solution for the overlayer dielectric function \( \varepsilon_o \) and thickness \( d \), as a general function of \( \rho \), and \( \theta \). However for a thin isotropic overlayer where \( d/\lambda \ll 1 \), the reflection coefficients can be written to the first order in \( d/\lambda \) as

\[ r_s(d) = r_s(0)\left(1 + \frac{4\pi id_{\omega,\perp}}{\lambda} \frac{\varepsilon_s - \varepsilon_o}{\varepsilon_s - \varepsilon_a}\right), \]  
(2.42)

\[ r_p(d) = r_p(0)\left(1 + \frac{4\pi id_{\omega,\perp}}{\lambda} \frac{(\varepsilon_s - \varepsilon_o)(1 - (\varepsilon_s/\varepsilon_o)\sin^2 \theta)}{\varepsilon_s - \varepsilon_a}\right). \]  
(2.43)

Then the ellipsometric reflection coefficient ratio \( \rho \) can be written as

\[ \rho(d) = \rho(0)\left(1 + \frac{4\pi id_{\omega,\perp}}{\lambda} \frac{\varepsilon_s(\varepsilon_s - \varepsilon_o)(\varepsilon_s - \varepsilon_a)}{\varepsilon_o(\varepsilon_s - \varepsilon_a)\varepsilon_s\cot^2 \theta - \varepsilon_s}\right). \]  
(2.44)

Using Eqs.(2.37) and (2.44) the pseudodielectric function \( \langle \varepsilon \rangle \) for a three-layer system with thin isotropic overlayer can be written as [6]
\[ \langle \varepsilon \rangle = \varepsilon_s + \frac{4\pi i d n_o}{\lambda} \varepsilon_s \left( \varepsilon_s - \varepsilon_o \right) \left( \varepsilon_o - \varepsilon_a \right) \left( \frac{\varepsilon_s}{\varepsilon_o} - \sin^2 \theta \right)^{1/2}. \] (2.45)

Furthermore by assuming \( |\varepsilon_s| \gg |\varepsilon_o| \gg |\varepsilon_a| = 1 \), this can be simplified to

\[ \langle \varepsilon \rangle \approx \varepsilon_s + \frac{4\pi i d}{\lambda} \varepsilon_s^{3/2}. \] (2.46)

Models involving anisotropic overayers are more complicated because electromagnetic waves traveling in anisotropic media split into normal modes that may involve projections along all three Cartesian coordinates. For an optically uniaxial material it is evident that the orientation of the principal axis affects the reflection and transmission coefficients of the electromagnetic waves in that medium. Since optical components such as retarders and polarizers are based on optically anisotropic materials, and in addition surfaces and interfaces of semiconductor materials are also generally optically anisotropic, I will consider the effects of anisotropy in further detail below.

### 2.5 Optical Diagnostics

In this section I describe the optical methods that we use to probe semiconductor films for both surface and bulk analysis. Reflectance Difference Spectroscopy (RDS) and Spectroscopic Ellipsometry/Polarimetry (SE) will be reviewed and equations for extracting sample parameters will be derived.

RDS and SE as currently performed are based on modulation of the reflected light intensity. Since the polarization state of the incident light is established before the beam interacts with the surface and is measured after reflection, we need to first establish a consistent coordinate system to describe the properties of both incident and reflected beams. Accordingly, we define a laboratory frame, and project the electromagnetic field vectors into this frame after passing the beam through each component of the system. We will also use local frames to describe the actions of the individual components. The laboratory frame is...
defined by the sample surface, with the z axis being the surface normal. To define the x and y axes we first define a central ray, which is defined mechanically by two irises on the entrance and two more on the exit sides of the sample. The central ray is taken to be that which passes through the irises when they are in their fully stopped-down positions. For weakly focused beams as used here, the actual beam consists of a bundle of rays passing in essentially through the system clustered about the central ray. The plane of incidence of the central ray defines laboratory x and y axes, the laboratory x axis being in the plane of incidence and the laboratory y axis perpendicular to it. Obviously, both x and y axes are in the plane of the surface. Although what we actually measure is the intensity of light emerging from the analyzer, the intensity is a result of a superposition and time-average of all fields emerging from the last optical element. Hence the entire problem can be addressed by considering one plane wave at a time, in the ideal case of a collimated beam evaluating the effect of each component on the field vector with a 2x2 matrix. The latter, the so-called Jones-Matrix representation, is a convenient way of representing the effect of each optical element on a given ray and in extended form will be used to describe and analyze both RDS and SE systems.

2.5.1 Reflectance-Difference Spectroscopy (RDS)

In reflectance-difference spectroscopy (RDS) the difference between the complex reflectances of light linearly polarized along the two principal axes at near-normal incidence is measured as a function of wavelength or energy. Since many semiconductors have cubic symmetry and are therefore optically isotropic in the bulk, one advantage of RDS is that it ignores the bulk contribution. However, because of reconstruction of the dangling bonds on the surface, in general the surface has a lower symmetry than the bulk and therefore has an anisotropic optical response. It is this anisotropic response that is measured in RDS.

Figure 2-5 shows RD spectra obtained for different reconstructions on (001)GaAs under different growth conditions [7]. Since GaAs is cubic, the bulk contribution to the RDS signal can be neglected compared to that of the surface. These data show that in principle RDS a powerful diagnostics tool to measure surface reconstructions. [8]
Figure 2-5 RD spectra of the primary reconstructions on (001) GaAs in UHV and AP H\textsubscript{2}. Sample temperatures for the UHV/H\textsubscript{2} ambients are indicated. (after ref.[7])

Figure 2-6 shows one possible configuration for performing RDS. This particular system uses an optical modulator and can also be considered a normal incidence ellipsometer.
Since one purpose of this work is to correlate the anisotropy spectra obtained of integrated RC/RS-PSCA system with normal incidence RDS spectra, I start with the derivation of the normal-incidence RDS system matrix and in particular its anisotropic part. The instrument can be described by Jones matrices, following the effect of each optical element on the x and y field components of a plane wave passing through the system. In this description I define a local coordinate system for each component and assume that the wave is propagating parallel to the z direction of each component. Then the Jones matrix for the system in Figure 2-6 can be written as
\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix} \begin{pmatrix} \cos M & -\sin M \\ \sin M & \cos M \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & e^{i\delta} \end{pmatrix} \begin{pmatrix} \cos M & \sin M \\ -\sin M & \cos M \end{pmatrix} \times \begin{pmatrix} r_x \\ 0 \end{pmatrix} \begin{pmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} E'_x \\ E'_y \end{pmatrix},
\] (2.47)

where \( P, M, \) and \( A \) are the azimuth angles of the polarizer, modulator, and analyzer respectively, with respect to plane of incidence; \( \delta \) is the relative retardation of the modulator, and \( r_x \) and \( r_y \) are the reflection coefficients parallel and perpendicular to the plane of incidence. The field that passes through the analyzer to the detector can be evaluated, and I find

\[
\mathbf{\tilde{E}} = \hat{x} E_x \left\{ \cos A'(r_x \cos M \cos P + r_y \sin M \sin P) + \sin A'(-r_x \sin M \cos P + r_y \cos M \sin P)e^{i\delta} \right\}
\]

where \( A' = (A-M) \). For \( A' = M = P = 45^\circ \), Eq.(2.48) simplifies significantly, and the field and intensity can be written as

\[
\mathbf{\tilde{E}} = \hat{x} \frac{E_x}{2\sqrt{2}} \left\{ (r_y + r_x) + (r_y - r_x)e^{i\delta} \right\},
\]

(2.49)

\[
I = \left| \mathbf{\tilde{E}} \right|^2 = \frac{|E_x|^2}{8} R^2 \left\{ 1 + \Re \left( \frac{(r_y - r_x)}{(r_y + r_x)/2}e^{i\delta} \right) \right\},
\]

(2.50)

\[
I = \left| \mathbf{\tilde{E}} \right|^2 = \frac{|E_x|^2}{8} \left| r_y + r_x \right|^2 \left\{ 1 + 2 \Re \left( \frac{(r_y + r_x)^2}{r_y + r_x} (r_y - r_x)e^{i\delta} \right) + \frac{r_y - r_x}{r_y + r_x} \right\}.
\]

(2.51)

Assuming \( r_y \approx r_x \), the third term in Eq.(2.51) can be neglected, and the expression for intensity is reduces to
where \( R^2 = |r_y + r_s|^2 \), and \( \frac{\Delta r}{r} = \frac{(r_y - r_s)}{(r_y + r_s)/2} \), where \( r \) is the complex reflectance coefficient, which can be written in terms of its magnitude and phase as \( r = |r|e^{i\theta} \). Then \( \frac{\Delta r}{r} = \frac{\Delta |r|}{|r|} + i\Delta \theta \) and

\[
I = \left| \mathbf{E} \right|^2 = \frac{|E_s|^2}{8} R^2 \left( 1 + \text{Re} \left( \frac{\Delta r}{r} e^{i\theta} \right) \right),
\]

which can be written in terms of Bessel functions:

\[
\cos \delta = \cos(\delta_0 \sin(\omega t)) = J_0(\delta_0) + 2 \sum_{n=1} \frac{J_{2n}(\delta_0)}{\delta_0} \cos(2n\omega t),
\]

\[
\sin \delta = \sin(\delta_0 \sin(\omega t)) = 2 \sum_{n=1} \frac{J_{2n-1}(\delta_0)}{\delta_0} \sin[(2n-1)\omega t].
\]

Therefore the intensity as an expansion in terms of harmonics of the modulation frequency is

\[
I = \left| \mathbf{E} \right|^2 = \frac{|E_s|^2}{8} R^2 \left( 1 + \frac{\Delta r}{r} \frac{J_0(\delta_0)}{\delta_0} - 2 \Delta \theta \sum_{n=1} \frac{J_{2n-1}(\delta_0)}{\delta_0} \sin[(2n-1)\omega t] \right).
\]

The next step is to use the three-layer model with an anisotropic overlayer to relate the RDS response to the material properties. Using Eqs.(2.91)-(2.93) (given in next section), at normal incidence the difference of reflectance coefficients between s- and p-polarizations of incoming light is
\[
\frac{\Delta r}{r} = 2 \frac{r_{pp}(0^\circ, 90^\circ) - r_{pp}(0^\circ, 0^\circ)}{r_{pp}(0^\circ, 90^\circ) - r_{pp}(0^\circ, 0^\circ)} = \frac{4\pi idn_a (\varepsilon_{xx} - \varepsilon_{yy})}{\lambda (\varepsilon_s - \varepsilon_a)} = \frac{\Delta |r|}{|r|} + i\Delta \theta.
\] (2.57)

From Eq.(2.57) the magnitude and phase can be written as

\[
\frac{\Delta |r|}{|r|} = -\frac{4\pi d n_a}{\lambda} \text{Im}\left(\frac{\varepsilon_{xx} - \varepsilon_{yy}}{\varepsilon_s - \varepsilon_a}\right),
\] (2.58)

\[
\Delta \theta = \frac{4\pi d n_a}{\lambda} \text{Re}\left(\frac{\varepsilon_{xx} - \varepsilon_{yy}}{\varepsilon_s - \varepsilon_a}\right).
\] (2.59)

The phase is generally neglected, so the important quantity that provides information about the surface is \(\Delta |r|/|r|\).

Because our integrated rotating sample rotating compensator (RSRC) polarizer-sample-compensator-analyzer (PSCA) SE system operates with the beam at non-normal incidence, we need to evaluate the effect of the anisotropy on parameters measured with this system and relate them back to the normal-incidence RDS signal. In Sec. 2.6.2 we cover the basic theory developed by hingerl et al., then apply it in Sec. 5.2.

### 2.5.2 Rotating Compensator Ellipsometer, Standard 2x2 Jones-matrix Theory

The main function of an ellipsometer is to detect the change in polarization state of light reflected from a sample. Information about the sample can then be extracted by modulating the reflected intensity so that it can be written as Fourier series. Coefficients of these Fourier series are then analyzed to obtain sample information as well as information needed to calibrate and align the instrument.
The fixed sample--rotating compensator ellipsometer of the polarizer-compensator-sample-analyzer (PCSA) configuration shown in Figure 2-7 is described in elementary form by the Jones matrix product

\[
\begin{pmatrix}
E_x' \\
E_y'
\end{pmatrix} = \begin{pmatrix}
1 & 0 \\
0 & 0
\end{pmatrix} \begin{pmatrix}
\cos A & \sin A \\
-\sin A & \cos A
\end{pmatrix} \begin{pmatrix}
r_p & 0 \\
0 & r_s
\end{pmatrix} \begin{pmatrix}
\cos C & -\sin C \\
\sin C & \cos C
\end{pmatrix} \begin{pmatrix}
1 & 0 \\
0 & e^{i\delta}
\end{pmatrix} \begin{pmatrix}
E_x \\
E_y
\end{pmatrix},
\]

(2.60)

where \( P, C, \) and \( A \) are the polarizer, compensator, and analyzer azimuths measured relative to the plane of incidence. In a rotating compensator system \( C = \omega t + \phi_c \), where \( \omega_c \) is the mechanical angular velocity and \( \phi_c \) is the phase. The compensator retardation is usually represented as a relative retardation \( \delta = \delta(\lambda) \), where \( \delta \) is actually is the relative phase of p- and s-polarized transmission coefficients of the compensator. For the MgF\(_2\) monoplate used in our system, it can either be calculated using the internal tilt angle of monoplate or extracted during the calibration routine.

By evaluating Eq.(2.60), we find that the reflected field reaching the detector is given by
\[
\hat{\mathbf{E}} = \hat{x} \frac{E'}{2} \left\{ (1 + e^{i\delta})(r_p \cos P \cos A + r_s \sin P \sin A) + \cos 2C(1 - e^{i\delta})(r_p \cos P \cos A - r_s \sin P \sin A) + \sin 2C(1 - e^{i\delta})(r_s \cos P \sin A + r_p \sin P \cos A) \right\},
\]

(2.61)

The intensity of the reflected light can therefore be written schematically in terms of zero, second and fourth harmonics as

\[
I = \left| \hat{\mathbf{E}} \right|^2 = \frac{|E'|^2}{4} \{ dc + a_2 \cos 2C + b_2 \sin 2C + a_4 \cos 4C + b_4 \sin 4C \},
\]

(2.62)

where the coefficients of these harmonics are given specifically as

\[
dc = \frac{|E'|^2}{4} \left\{ 2 \left| r'_p \right|^2 + \left| r'_s \right|^2 \right\} + \left( \left| r'_p \right|^2 - \left| r'_s \right|^2 \right)(1 + \cos \delta) \cos 2P + 2 \Re(r''_p r'_s)(1 + \cos \delta) \sin 2P \},
\]

(2.63)

\[
a_2 = -\left| E'_s \right|^2 \sin \delta \Im(r''_p r'_s) \sin 2P,
\]

(2.64)

\[
b_2 = \left| E'_s \right|^2 \sin \delta \Im(r''_p r'_s) \cos 2P,
\]

(2.65)

\[
a_4 = \frac{|E'|^2}{4} (1 - \cos \delta) \left( \left| r'_p \right|^2 - \left| r'_s \right|^2 \right) \cos 2P - 2 \Re(r''_p r'_s) \sin 2P \},
\]

(2.66)

\[
b_4 = \frac{|E'|^2}{4} (1 - \cos \delta) \left( \left| r'_p \right|^2 - \left| r'_s \right|^2 \right) \sin 2P + 2 \Re(r''_p r'_s) \cos 2P \},
\]

(2.67)

where \( r'_p = r_p \cos A, r'_s = r_s \sin A. \)

The intensity can be eliminated by normalizing the coefficients:

\[
\alpha_{2,4} = \frac{a_{2,4}}{dc},
\]

(2.68)
\[
\beta_{2,4} = \frac{b_{2,4}}{dc}
\]  

Since these depend on \( \rho = r_p/r_s \), we can use the coefficients to extract \( \Psi \) and \( \Delta \) from the normalized 2\(^{\text{nd}}\) and 4\(^{\text{th}}\) harmonic terms. However, the number of constraints (equations) exceeds the number of unknowns (4 equations, 2 unknowns). We solve this problem by using a nonlinear least-squares routine to best-fit the model expressions to the measured normalized coefficients using the real and imaginary parts of \( \rho \) as adjustable parameters. The advantage of the least-squares procedure is that it places the most weight on the coefficients that are most relevant for a given set of conditions. Thus the complete disappearance of the 2\(^{\text{nd}}\) harmonic term at \( \delta = 180^\circ \) (compensator functioning as a half-wave plate) is not a fatal error. The last step is to use Eq.(2.37) to obtain the pseudodielectric function of the substrate.

### 2.5.3 Integrated System

While the PCSA-RCE or PSCA-RCE with a fixed substrate gives considerably more accurate results than its rotating-analyzer or rotating-polarizer predecessors, it does not provide any information about sample anisotropy. However, this information can be obtained by rotating the sample phase-coherently with the compensator, as done with the rotating sample-rotating compensator PSCA configuration as shown in Figure 2-8. The details of this system have been given elsewhere [9,10], so I provide only a summary here.
The light source for the system is a Xe short-arc lamp. The light is focused onto the sample over a path length of about 1 m after passing through the polarizer, which is a quartz Rochon prism. The reflected light then passes through the rotating compensator and a quartz-Rochon analyzer prism, and is focused onto the entrance slit of a spectrometer. The spectrometer is equipped with a photodiode-array (PDA) detector that can acquire complete spectra from 230 to 840 nm in approximately 5 ms increments at a resolution of 1024 pixels. Data acquisition is triggered off the rotating compensator, with 25 spectra being obtained for each mechanical rotation of the compensator. These spectra are then Fourier-transformed to obtain the coefficients actually used for analysis as

\[ I = dc + \sum_{n=1} a_n \cos n\omega t + b_n \sin n\omega t. \]  (2.70)
The ellipsometric data are extracted from the $0_{\omega t}$, $2_{\omega t}$ and $4_{\omega t}$ coefficients. Information about system alignment is provided by the $1_{\omega t}$, $3_{\omega t}$, and $5_{\omega t}$ coefficients, while the $8_{\omega t}$ coefficients provide information about system linearity.

A typical intensity spectrum, here taken with (110)Si sample at room temperature, is shown in Figure 2-9. The data are plotted as a function of pixel number of the photodiode array, which yields a scale linearly proportional to wavelength.

![Intensity of PSCA Ellipsometer](image)

*Figure 2-9 Transmitted intensity measured detected for a (110)Si sample as a function of PDA pixel number. The structure in the midrange is due to spectral line emission from Xe arc lamp.*
The sample rests on a mount that is indirectly heated to allow the sample temperature to be varied. The sample mount in turn is fastened to a spindle that rotates at approximately 1200 rpm to pump gas over the surface of the sample and ensure more uniform growth. The sample tilt can be adjusted during operation to eliminate runout, and important consideration for optical measurements.

The key to acquiring sample-anisotropy data is to synchronize the rotation of the spindle and the compensator. We use a 5:1 ratio, which at the standard 1200 rpm rotation rate of the spindle leads to a data acquisition rate of 4 Hz. Since the surface anisotropy has π symmetry, this leads to a $10\omega t$ contribution to the detected intensity that yields the anisotropy spectrum of the material as discussed below. Synchronization is necessary not only to determine the sample anisotropy, but also to eliminate pseudonoise, since with anisotropic samples different sample azimuth angles yield different values of $\rho$. The specific choice of 5:1 also prevents the sidebands of the $10\omega t$ anisotropy contribution from overlapping with any of the other coefficients and therefore compromising the data. The complete system allows us to obtain information on anisotropy as well as sample ellipsometric quantities using a single optical beam.

The main element of an RCE is the compensator, so a brief discussion is in order. Excluding achromatic types, which generally are not suitable for accurate measurements, there are three main types of compensators: the biplate compensator, the Berek compensator [11,12], and the monoplate compensator [13]. Biplate compensators are fabricated from two parallel plates of crystal quartz or MgF$_2$, with the fast axes of the plates perpendicular to each other and internally aligned so that their surface normal vectors are parallel to the rotation axis. The two plates generally have a thickness difference of about 14 µm, which is the thickness that a zero-order plate would have if it were to be useful from an optical perspective. Since a 14 µm thick plate is too fragile for actual application, it is simulated by the combination. However, any azimuthal misalignment of the principal axes of the two plates leads to oscillations in the relative retardation that vary rapidly with wavelength [14]. Moreover, for crystal quartz the plates should ideally be of opposite handedness, which is not
often achievable. Finally, the beams transmitted by the biplate are affected adversely by multiple internal reflections. Consequently, the biplate is a poor choice for the compensator.

One alternative is the Berek compensator [12], which is fabricated with the c-axis normal to the surface. To obtain a relative retardation, the entire plate is inclined. This allows the use of a relatively thick plate, typically of the order of 500 µm, for mechanical strength while allowing for zero-order operation. In addition, the relative retardation can be adjusted by adjusting the tilt angle of the plate. However, the Berek plate has the disadvantage that it laterally displaces the beam, a result of refraction at the tilted interface combined with propagation of the refracted beam through the component.

The difficulties with the Berek plate can be circumvented by cutting the crystal so the c axis is tilted internally by the amount needed to get the desired relative retardation, typically near 7°. The resulting monoplate compensator allows zero-order operation with essentially no lateral displacement of the beam. For these reasons we use monoplate compensators. The disadvantage of the monoplate is that it is mathematically more difficult to model and analyze. One of the objectives of this thesis is to perform this analysis and eliminate this disadvantage.

### 2.6 Elementary Treatments of Anisotropy

#### 2.6.1 4x4 Matrix Method

To obtain transmission and reflection coefficients using multiple-layer models, we must first determine the electromagnetic fields inside each layer, and in particular their normal modes, by solving the dispersion equation. We next take into account the boundary conditions at each interface. Writing the relevant fields as vectors we can express the boundary conditions as
Figure 2-10 Schematic diagram defining the fields used in the application of 4x4 methods to multiple layers. Transmitted and reflected fields and internal boundaries for three layers are shown.

\[
\varepsilon_1 (E_{tt} + E_{rt}) \cdot \hat{n}_{ll} = \varepsilon_2 (E_{t2} + E_{r2}) \cdot \hat{n}_{ll} \tag{2.71}
\]

\[
(k_{r1} \times E_{tt} + k_{r1} \times E_{rt}) \cdot \hat{n}_{ll} = (k_{r2} \times E_{t2} + k_{r2} \times E_{r2}) \cdot \hat{n}_{ll} \tag{2.72}
\]

\[
(E_{tt} + E_{rt}) \times \hat{n}_{ll} = (E_{t2} + E_{r2}) \times \hat{n}_{ll} \tag{2.73}
\]

\[
(k_{r1} \times E_{tt} + k_{r1} \times E_{rt}) \times \hat{n}_{ll} = (k_{r2} \times E_{t2} + k_{r2} \times E_{r2}) \times \hat{n}_{ll} \tag{2.74}
\]

where the quantities are defined in Figure 2-10. Equations (2.71) and (2.72) represent the conditions on the normal components of the displacement field and magnetic flux density, whereas Eqs. (2.73) and (2.74) state the conditions on the tangential components of E and H. The same conditions apply to other layers as well. The fact that Eqs. (2.71) – (2.74) appear to represent 6 conditions on 4 coefficients is not a problem, because it is straightforward to show that Eqs. (2.71) and (2.72) are already contained in Eqs. (2.73) and (2.74). Thus at a given boundary we need consider only the last two equations.
The left and right sides of Eqs. (2.73) and (2.74) can be represented by a 4x4 matrix. This method was first developed by Berreman [15]. If all layers are isotropic, the solutions are easy to find since the Cartesian components separate and the normal modes are self-evident. However, if a material is anisotropic the individual Cartesian components of the fields in the material are generally related, so a simple Cartesian-component separation is not possible. This complication can be accommodated by using projection matrices that take the normal-mode coefficients back to the respective Cartesian components, as I will discuss in the next chapter. However, these considerations also show that uncoupled p- or s-polarized waves arriving at the boundary will become coupled as a result of transmission the anisotropic layer. This more general case has been described by Yeh [16].

However the Yeh formulation is deficient in that, depending on the relative orientations of the propagation vectors and the crystal axes, the solutions of the dispersion equation for the normal modes have singularities (Figure 2-11). In the next chapter I will show how these singularities can be eliminated by evaluating multiple mode vectors by the method of expansion by minors, then choosing the eigenvector with largest normalization coefficient.

![Figure 2-11 Orientation of crystal axes and reference laboratory frame.](image)
Returning to the original problem, since we only need the tangential components of the boundary equations, with the reference frame and plane of incidence selected, Eqs.(2.73) and (2.74) can be rewritten by separating to its components as

\[
\left[ \left( (E_{ti} + E_{ri}) \times \hat{z} \right) \hat{x} + \left( (E_{ti} + E_{ri}) \times \hat{z} \right) \hat{y} \right]_{l2} = \\
\left[ \left( (E_{t2} + E_{r2}) \times \hat{z} \right) \hat{x} + \left( (E_{t2} + E_{r2}) \times \hat{z} \right) \hat{y} \right]_{l2},
\]

\( k E_{ti} + k E_{ri} \) (2.75)

\[
\left[ \left( (k_{t1} \times E_{ti} + k_{r1} \times E_{ri}) \times \hat{z} \right) \hat{x} + \left( (k_{t1} \times E_{ti} + k_{r1} \times E_{ri}) \times \hat{z} \right) \hat{y} \right]_{l2} = \\
\left[ \left( (k_{t2} \times E_{t2} + k_{r2} \times E_{r2}) \times \hat{z} \right) \hat{x} + \left( (k_{t2} \times E_{t2} + k_{r2} \times E_{r2}) \times \hat{z} \right) \hat{y} \right]_{l2}.
\]

(2.76)

Let the external field vectors be represented with s and p components as

\[
E_{\alpha} = E_{\alpha s} e^{i\mathbf{k}_{\alpha s} \cdot \mathbf{r}} \hat{\mathbf{e}}_{\alpha s} + E_{\alpha p} e^{i\mathbf{k}_{\alpha p} \cdot \mathbf{r}} \hat{\mathbf{e}}_{\alpha p},
\]

(2.77)

where s and p are defined relative to the sample normal and where \( \alpha = t1, r1, t2, r2 \). Then the left hand side of above equations can be written in a matrix form as

\[
\begin{pmatrix}
\hat{\mathbf{e}}_{t1s} \cdot \hat{\mathbf{y}} & \hat{\mathbf{e}}_{r1s} \cdot \hat{\mathbf{y}} & \hat{\mathbf{e}}_{t1p} \cdot \hat{\mathbf{y}} & \hat{\mathbf{e}}_{r1p} \cdot \hat{\mathbf{y}} \\
(\mathbf{k}_{t1s} \times \hat{\mathbf{e}}_{t1s}) \cdot \hat{\mathbf{x}} & (\mathbf{k}_{r1s} \times \hat{\mathbf{e}}_{r1s}) \cdot \hat{\mathbf{x}} & (\mathbf{k}_{t1p} \times \hat{\mathbf{e}}_{t1p}) \cdot \hat{\mathbf{x}} & (\mathbf{k}_{r1p} \times \hat{\mathbf{e}}_{r1p}) \cdot \hat{\mathbf{x}} \\
\hat{\mathbf{e}}_{t1s} \cdot \hat{\mathbf{x}} & \hat{\mathbf{e}}_{r1s} \cdot \hat{\mathbf{x}} & \hat{\mathbf{e}}_{t1p} \cdot \hat{\mathbf{x}} & \hat{\mathbf{e}}_{r1p} \cdot \hat{\mathbf{x}} \\
(\mathbf{k}_{t1s} \times \hat{\mathbf{e}}_{t1s}) \cdot \hat{\mathbf{y}} & (\mathbf{k}_{r1s} \times \hat{\mathbf{e}}_{r1s}) \cdot \hat{\mathbf{y}} & (\mathbf{k}_{t1p} \times \hat{\mathbf{e}}_{t1p}) \cdot \hat{\mathbf{y}} & (\mathbf{k}_{r1p} \times \hat{\mathbf{e}}_{r1p}) \cdot \hat{\mathbf{y}}
\end{pmatrix}
\begin{pmatrix}
e^{\mathbf{k}_{t1s} \cdot \mathbf{r}} 0 0 0 \\
e^{\mathbf{k}_{r1s} \cdot \mathbf{r}} 0 0 0 \\
e^{\mathbf{k}_{t1p} \cdot \mathbf{r}} 0 0 0 \\
e^{\mathbf{k}_{r1p} \cdot \mathbf{r}} 0 0 0
\end{pmatrix}
\begin{pmatrix}
E_{t1s} \\
E_{r1s} \\
E_{t1p} \\
E_{r1p}
\end{pmatrix}.
\]

(2.78)

The right side of Eqs.(2.75) and (2.76) can be written in the same manner. The first matrix in Eq.(2.78) is called the dynamic matrix, \( \mathbf{D} \) and contains information about the medium. The second matrix is called the propagation matrix, \( \mathbf{P} \). Since all other components in \( \mathbf{P} \) are the same throughout the boundary, only the z-component of the propagation vector is needed. The 4x1 vector \( \mathbf{E} \) describes the magnitude of fields in that medium.

Using the 4x4 matrix method, the two-layer problem can be solved by writing
\[ \mathbf{D}_s \cdot \mathbf{P}_s \cdot \mathbf{E}_s = \mathbf{D}_a \cdot \mathbf{P}_a \cdot \mathbf{E}_a, \]  
(2.79)

\[ \mathbf{E}_a = (\mathbf{P}_a^{-1} \cdot \mathbf{D}_a^{-1} \cdot \mathbf{D}_s \cdot \mathbf{P}_s) \cdot \mathbf{E}_s, \]  
(2.80)

\[ \mathbf{S} = \mathbf{P}_a^{-1} \cdot \mathbf{D}_a^{-1} \cdot \mathbf{D}_s \cdot \mathbf{P}_s. \]  
(2.81)

The matrix \( \mathbf{S} \) is called the system transfer matrix, and multiple layers can be representing by adding propagation and dynamic matrices in the corresponding order [16]. Details can be found in the references given. Since the primary boundary condition (no back-reflected wave) is at the exit side of the structure, the problem is usually worked backward with the inverses of the matrices above, calculating the incident and reflected fields in terms of the transmitted fields. Then the secondary boundary condition (incident s- or p-polarized field) is applied and the transmitted amplitude normalized out. Following this procedure schematically the reflection coefficients are then given as

\[ r_{ss} = \frac{E_{rs}}{E_{ss}} = \frac{S_{21}S_{33} - S_{23}S_{31}}{S_{11}S_{33} - S_{13}S_{31}}, \]  
(2.82)

\[ r_{sp} = \frac{E_{rs}}{E_{sp}} = \frac{S_{33}S_{11} - S_{21}S_{13}}{S_{11}S_{33} - S_{13}S_{31}}, \]  
(2.83)

\[ r_{ps} = \frac{E_{rp}}{E_{ss}} = \frac{S_{43}S_{11} - S_{41}S_{13}}{S_{11}S_{33} - S_{13}S_{31}}, \]  
(2.84)

\[ r_{pp} = \frac{E_{rp}}{E_{sp}} = \frac{S_{43}S_{11} - S_{41}S_{13}}{S_{11}S_{33} - S_{13}S_{31}}, \]  
(2.85)

where \( E_{ra} \) and \( E_{sa} \) (\( \alpha = s, p \)) are reflected and substrate (transmitted) waves with perpendicular and parallel to the plane of incidence.

The 4x4 matrix method is useful for analyzing multiple layer models analytically, but to obtain the dynamic and propagation matrices it is necessary to first calculate the
propagation and wave vectors in that layer. It is useful to start with Yeh’s [16] formulation. In the next chapter I show that this solution can be expanded such that the solution for the anisotropic model can be reduced to isotropic cases without any singularity in the 4x4 matrix and as a result can be used directly in numerical analysis.

The dispersion relation depends on the dielectric function of the material and can be expanded into three scalar equations and written in matrix form. This will be referred to as the dispersion matrix. For the monoplate I begin by writing a dielectric tensor rotated into the laboratory frame as

\[
e_{\text{lab}} = \begin{pmatrix}
e_{xx} & e_{xy} & e_{xz} \\
e_{xy} & e_{yy} & e_{yz} \\
e_{xz} & e_{yz} & e_{zz}
\end{pmatrix}.
\] (2.86)

Substituting this into the dispersion equation, I obtain the dispersion equation in matrix form:

\[
\begin{pmatrix}
\frac{\omega^2}{c^2} e_{xx} - k_y^2 - k_z^2 \\
\frac{\omega^2}{c^2} e_{xy} + k_x k_y \\
\frac{\omega^2}{c^2} e_{xz} + k_x k_z
\end{pmatrix}
\begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix} = 0.
\] (2.87)

The nontrivial solution requires that the determinant of dispersion matrix vanishes. For a wave plate whose surface normal is not parallel to the rotation axis of the plate the result is a quartic equation in \(k_z\) with complex coefficients, instead of the usual quadratic equation for \(k_z^2\). When the solution is substituted back into Eq.(2.87) the wave vectors are found as
\[
E_i = N_i \left( \begin{array}{c}
\left( \frac{\omega^2}{c^2} \epsilon_{yy} - k_x^2 - k_{z,i}^2 \right) - \left( \frac{\omega^2}{c^2} \epsilon_{zz} - k_z^2 - k_{z,i}^2 \right)
\left( \frac{\omega^2}{c^2} \epsilon_{xy} + k_y k_{z,i} \right)
\left( \frac{\omega^2}{c^2} \epsilon_{xz} + k_x k_{z,i} \right)
\left( \frac{\omega^2}{c^2} \epsilon_{yz} + k_y k_{z,i} \right)
\left( \frac{\omega^2}{c^2} \epsilon_{zy} + k_y k_{z,i} \right)
\left( \frac{\omega^2}{c^2} \epsilon_{zx} + k_x k_{z,i} \right)
\left( \frac{\omega^2}{c^2} \epsilon_{zy} - k_z^2 - k_{z,i}^2 \right)
\end{array} \right) \right),
\]

where \( k_{z,i} \) is z-component of the transmitted and reflected propagation vector with \( i = 1, 2, 3, 4 \).

In the next chapter special cases and a general solution involving both isotropic and anisotropic substrates will be given, along with their application to the monoplate retarder.

**2.6.2 Thin Anisotropic Overlayer**

In an anisotropic layer, the s- and p-polarized modes of the incident wave couple into polarization states that are neither s nor p. Thus the states mix. In general the reflected wave must therefore be written as

\[
E_{rp} = r_{pp} E_{ip} + r_{ps} E_{is},
\]

\[
E_{rs} = r_{ss} E_{is} + r_{sp} E_{ip},
\]

so the reflection matrix has off-diagonal components. Analytical expressions for the complex reflectance coefficients coupled to first order in \( d/\lambda \) have been derived by Hingerl et al. [17] for the three-layer model with isotropic substrate:

\[
r_{ss} = r_{ss}^0 \left( 1 + \frac{4 \pi i d n_{a\perp}}{\lambda} \frac{\epsilon_s - \Delta \epsilon \cos 2\phi}{\epsilon_s - \epsilon_a} \right),
\]
where $\varepsilon = (\varepsilon_y + \varepsilon_x)/2$ and $\Delta \varepsilon = (\varepsilon_y - \varepsilon_x)/2$ and $\phi$ is the angle between the plane of incidence and the x-axis of the sample. The rest of the notation follows from two-layer model calculations, Eqs.(2.35) and (2.36). I will use these results with the system Jones-matrix for the RSRC-PSCA ellipsometer to extract anisotropy information and obtain an analytical solution to the first order, a result that otherwise would have to be obtained by numerical methods.
Chapter 3

3 EXTENDING EXISTING TREATMENTS FOR ANISOTROPIC SYSTEMS

3.1 Thin Anisotropic Overlayers: A Taylor-Series Approach

For extremely thin layers one method that appears not to have been explored previously is the use of a Taylor series expansion for describing propagation from the ambient through the layer to the bulk. This approach has the advantage that the dispersion equation does not have to be solved for either the wave vectors or the corresponding normal modes. Thus I bypass completely the complications that arise as a result of double or degenerate root in the dispersion equation. Although the results obtained are the same as those of Hingerl et al., the calculation is interesting not only because it avoids the dispersion equation and its associated complications, but also because it requires an unusual number of boundary conditions. Since it also appears not to have been given before, I will give a brief description of the method.

Basically we simply write

\[ e^{ikr} = (1 + ik_x x + ik_z z) \]  \hspace{1cm} (3.1)
Since we know the \( \mathbf{E} \) and \( \mathbf{B} \) fields for the ambient and bulk layers, we can also define \( \hat{\mathbf{E}} \) and \( \hat{\mathbf{B}} \) in the overlayer similarly as

\[
\hat{\mathbf{E}} = \hat{x}\left( E_{x_0} + E_{x_1} x + E_{x_2} y + E_{x_2} z \right) + \hat{y}\left( E_{y_0} + E_{y_1} x + E_{y_2} y + E_{y_2} z \right) + \hat{z}\left( E_{z_0} + E_{z_1} x + E_{z_2} y + E_{z_2} z \right),
\]

(3.2)

\[
\hat{\mathbf{B}} = \hat{x}\left( B_{x_0} + B_{x_1} x + B_{x_2} y + B_{x_2} z \right) + \hat{y}\left( B_{y_0} + B_{y_1} x + B_{y_2} y + B_{y_2} z \right) + \hat{z}\left( B_{z_0} + B_{z_1} x + B_{z_2} y + B_{z_2} z \right).
\]

(3.3)

There are 26 boundary equations, 8 of which is called the interior condition, that is the Maxwell equations inside the overlayer, and 18 equation results from applying the continuity of normal and tangential components at the interfaces. 24 of these 26 equaitons are independent and this corresponds to the 24 unknowns in the above expressions. After finding these 24 coefficients, we obtain the fields at \( z = d \), after which the solution proceeds as with any 2-layer system.

Results are the same obtained by Hingerl et al.. The same procedure can also be applied to the transmission through thin anisotropic layers. Since we do not require solving for propagation vectors in the overlayer, this eliminates the zero length field vector, thus any singularity of inverting matrix representations of interfaces. Since boundary conditions at the interfaces have been discussed before, it will not be given here.

### 3.2 Crystal Optics: Dielectric Response of Anisotropic Systems

#### 3.2.1 Solution of Dispersion Equation

Equation (2.88) is a general solution for a wave vector in an anisotropic material. It can be inserted in to the 4x4 dynamic matrix Eq.(2.78) and used in the general system matrix defining the multilayer problem. However, to be able to use this solution in the 4x4 method all four roots of the quartic equation derived from dispersion matrix should be discrete.
Furthermore, since this quartic equation is usually solved numerically and analytical solutions are not very useful, depending on reducing the quartic equation to a lower degree polynomial, there is always the possibility that the determinant of the dynamic matrix is zero, which therefore makes the system matrix singular. A mathematical solution having an indeterminate wave vectors is unacceptable from both mathematical and physical grounds since it would give a singularity in the system matrix solution for a multilayer problem.

Therefore we need to formulate a general solution that avoids singularities in the solution of the 4x4 system matrix and that can be applied to both isotropic and anisotropic materials. To do this we use a theorem from matrix algebra.

To set up the problem I assume an anisotropic layer in which the reference axes are defined with the z-axis corresponding to the surface normal, and the x-z plane being the plane of incidence as shown in Figure 3-1.

\[
\begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_b & 0 \\
0 & 0 & \varepsilon_c \\
\end{pmatrix},
\]

(3.4)
where \( \varepsilon_a, \varepsilon_b, \varepsilon_c \) are dielectric responses for electric fields along the x-, y-, and z-axes respectively with respect to the crystal reference frame. These responses may be complex and depend on energy of incoming light. Let \( \phi \) be the azimuthal angle with respect to the x-axis.

Then in the laboratory frame the dielectric tensor becomes

\[
\epsilon_{lab} = \begin{pmatrix}
\epsilon + \Delta \varepsilon \cos 2\phi & \Delta \varepsilon \sin 2\phi & 0 \\
\Delta \varepsilon \sin 2\phi & \varepsilon - \Delta \varepsilon \cos 2\phi & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix},
\]

(3.5)

and

\[
\epsilon_{lab} = \begin{pmatrix}
\cos \phi & -\sin \phi & 0 \\
\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\epsilon_a & 0 & 0 \\
0 & \epsilon_b & 0 \\
0 & 0 & \epsilon_c
\end{pmatrix}
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix},
\]

(3.6)

where \( \varepsilon = (\epsilon_a + \epsilon_b)/2, \Delta \varepsilon = (\epsilon_a - \epsilon_b)/2 \).

The next step is to find the propagation vector in this anisotropic layer. The dispersion relation can be expanded into three scalar equations and written in matrix form, which is the dispersion matrix. Substituting the dielectric tensor (Eq.(3.6)) into the dispersion relation (Eq.(2.34)), neglecting as usual the magnetic permeability, and taking since xz is plane of incidence, the dispersion matrix becomes

\[
\begin{pmatrix}
\frac{\omega^2}{c^2} (\varepsilon + \Delta \varepsilon \cos 2\phi) - k_z^2 \\
\frac{\omega^2}{c^2} \Delta \varepsilon \sin 2\phi \\
k_x k_z
\end{pmatrix}
\begin{pmatrix}
k_x \\
k_z \\
k_x k_z
\end{pmatrix}
\begin{pmatrix}
0 \\
k_x k_z \\
k_x k_z
\end{pmatrix}
\begin{pmatrix}
\epsilon_x \\
\epsilon_y \\
\epsilon_z
\end{pmatrix}
= \begin{pmatrix}
0 \\
0 \\
0
\end{pmatrix},
\]

(3.7)

For these equations to have a nontrivial solution, the determinant of the dispersion matrix must equal zero. Solving the determinant for \( k_z^2 \), we get
\[ k_z^2 = \frac{\omega^2}{c^2} \gamma_{1,2}, \]  

(3.8)

where

\[ \gamma_{1,2} = \varepsilon - \frac{1}{2} \left( 1 + \frac{\varepsilon + \Delta \varepsilon \cos 2\phi}{\varepsilon_c} \right) \sin^2 \theta \mp \]

\[ \left\{ \Delta \varepsilon^2 + \left[ \frac{1}{2} \left( 1 - \frac{\varepsilon + \Delta \varepsilon \cos 2\phi}{\varepsilon_c} \right) \sin^2 \theta \right] - \frac{\Delta \varepsilon}{\varepsilon_c} \left( \Delta \varepsilon + (\varepsilon - \varepsilon_c) \cos 2\phi \right) \sin^2 \theta \right\}^{1/2}. \]  

(3.9)

Then \( k_{z,i} = \pm \frac{\omega}{c} \sqrt{\gamma_{1,2}} \), where \( i = 1, 2, 3, 4 \) represents the two modes in both reflected and transmitted form. Here the minus sign represents transmission and the plus sign reflection.

For the configuration defined above using Yeh’s solution, the wave vector from Eq.(2.88) is

\[ E_i = N_i \begin{pmatrix} (\varepsilon - \Delta \varepsilon \cos 2\phi - \sin^2 \theta - \gamma_{1,2}^2) n_{\perp}^2 & -n_{\perp}^2 \Delta \varepsilon \sin 2\phi & \pm \sin \theta \sqrt{\gamma_{1,2}^2 (\varepsilon - \Delta \varepsilon \cos 2\phi - \sin^2 \theta - \gamma_{1,2}^2)} \end{pmatrix}, \]  

(3.10)

where \( n_{\perp} = \sqrt{\varepsilon_c - \sin^2 \theta} \). It follows immediately from Eq.(3.10) that one of the solutions becomes zero for \( \phi = 0 \). Therefore the corresponding dynamic matrix becomes singular and cannot be inverted. In the next section I present a solution that mode vectors do not vanish at the same time.

### 3.2.2 Determination of Normal Modes: Elimination of Singularities

When \( \phi = \pi/2 \) the other solution in Eq.(3.10) also becomes zero. Since zero these solutions are not physical, we need to find the physical solution that satisfies the dispersion relation. We can do this as follows. We write a general 3x3 dispersion matrix as

\[ \ldots \]
\[
\begin{pmatrix}
m_{11} & m_{12} & m_{13} \\
m_{21} & m_{22} & m_{23} \\
m_{31} & m_{32} & m_{33}
\end{pmatrix}, \quad (3.11)
\]

Since the determinant of this expression is zero, we can assign any row to be a "principal" row and evaluate the determinant by expanding the remaining two rows as minors multiplying the values in the "principal" row. Now the normal modes also satisfy the same equation. Hence we can simply identify the minors with the components of the normal mode. This is an application of the well known matrix theorem from matrix algebra which states that the components of the eigenvectors also satisfy the dispersion equation.

Since any of the three rows can be considered a "principal" row, for any given eigenvalue we can write the mode vector corresponding to the eigenvalue in 3 different ways, each of which satisfies the dispersion equation:

\[
E_1 = N_1 \begin{pmatrix} m_{22}m_{33} - m_{23}m_{32} \\ -(m_{12}m_{33} - m_{13}m_{31}) \\ m_{12}m_{32} - m_{12}m_{31} \end{pmatrix}, \tag{3.12}
\]

\[
E_2 = N_2 \begin{pmatrix} m_{12}m_{33} - m_{13}m_{32} \\ -(m_{11}m_{33} - m_{13}m_{31}) \\ m_{11}m_{32} - m_{11}m_{31} \end{pmatrix}, \tag{3.13}
\]

\[
E_3 = N_3 \begin{pmatrix} m_{12}m_{23} - m_{13}m_{22} \\ -(m_{11}m_{23} - m_{13}m_{21}) \\ m_{11}m_{22} - m_{11}m_{21} \end{pmatrix}, \tag{3.14}
\]

where the Ni are normalization factors. As mentioned above, because the determinant vanishes all three solutions satisfy the dispersion relation. However, all three never go to zero at the same time. Hence singularities in the matrix calculations can be avoided simply by evaluating the three possibilities then choosing that which has the longest length, defined as the sum of the absolute squares of the three components.
Specifically, for the example configuration of crystal axis given above, the three different forms of the mode vector can be written in three different ways as

\[
E_{1,i} = \begin{cases} 
    \left[ \left( \varepsilon - \Delta \varepsilon \cos 2\phi \right) - \sin^2 \theta - \gamma_i \right] n_{c\perp}^2 \\
    -\Delta \varepsilon \sin 2\phi \ n_{c\perp}^2 \\
    \pm \left[ \left( \varepsilon - \Delta \varepsilon \cos 2\phi \right) - \sin^2 \theta - \gamma_i \right] \sin \theta \sqrt{\gamma_i} 
\end{cases}, 
\]

(3.15)

\[
E_{2,i} = \begin{cases} 
    \Delta \varepsilon \sin 2\phi \ n_{c\perp}^2 \\
    - \left[ \left( \varepsilon + \Delta \varepsilon \cos 2\phi \right) - \gamma_i \right] n_{c\perp}^2 + \sin^2 \theta \gamma_i \\
    \pm \Delta \varepsilon \sin 2\phi \ \sin \theta \sqrt{\gamma_i} 
\end{cases}, 
\]

(3.16)

\[
E_{3,i} = \begin{cases} 
    \pm \sin \theta \sqrt{\gamma_i} \left[ \left( \varepsilon - \Delta \varepsilon \cos 2\phi \right) - \sin^2 \theta - \gamma_i \right] \\
    \mp \Delta \varepsilon \sin 2\phi \ \sin \theta \sqrt{\gamma_i} \\
    \left[ \left( \varepsilon + \Delta \varepsilon \cos 2\phi \right) - \gamma_i \right] \left[ \left( \varepsilon - \Delta \varepsilon \cos 2\phi \right) - \sin^2 \theta - \gamma_i \right] - \Delta \varepsilon^2 \sin^2 2\phi 
\end{cases}, 
\]

(3.17)

where first sign above is for transmission and second for reflection. Here \( \gamma_i, \ i=1,2,3,4 \) is used for transmitted and reflected z-component of the propagation vector with the factor \( \omega/c \) removed for simplicity.

All three solutions must be considered because for mathematical reasons each of the three vanishes at some particular value of \( \phi, \theta \) or dielectric-tensor components. Table 3-1 shows the conditions for which the above modes vanish.
Table 3-1. Azimuths for which each of three wave vectors vanish for different propagation vectors. Note there are no conditions where all go to zero at the same time.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Azimuth</th>
<th>$k_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_1 = [0,0,0]$</td>
<td>$\phi = 0$</td>
<td>$k_{z,1}$</td>
</tr>
<tr>
<td>$E_1 = [0,0,0]$</td>
<td>$\phi = \pi / 2$</td>
<td>$k_{z,2}$</td>
</tr>
<tr>
<td>$E_2 = [0,0,0]$</td>
<td>$\phi = 0$</td>
<td>$k_{z,2}$</td>
</tr>
<tr>
<td>$E_2 = [0,0,0]$</td>
<td>$\phi = \pi / 2$</td>
<td>$k_{z,1}$</td>
</tr>
<tr>
<td>$E_3 = [0,0,0]$</td>
<td>$\phi = 0$</td>
<td>$k_{z,1}$</td>
</tr>
<tr>
<td>$E_3 = [0,0,0]$</td>
<td>$\phi = \pi / 2$</td>
<td>$k_{z,2}$</td>
</tr>
</tbody>
</table>

Therefore by working with all three, and choosing the largest, we avoid the singularities in subsequent calculations that would result when the length of any single one vanishes. This mathematical difficulty, which is probably not uncommon, cannot be anticipated from the article of Yeh [16].
Chapter 4

4 AXIALLY MISALIGNED COMPONENTS, BASIC CHARACTERISTICS

In this section, the effect of axial misalignment of ellipsometer components will be analyzed, with particular emphasis on the monoplate compensator. Optical systems are generally designed by first assuming that the system behaves ideally. Calibration and alignment procedures are then established to determine initial system parameters including component misalignments and nonlinearities. These system errors generally appear as effects periodic in component rotation and in addition tend to have characteristic spectral dependences. They can be due either to manufacturing errors that may not be possible to correct, or from component misalignment. In either case they must be determined and the data corrected for their presence. Fortunately, for most purposes a first-order approach is adequate, so analytic results can be obtained.

The polarizer, compensator, and analyzer are the primary components of any optical-diagnostics tool that has the objective of determining the change of polarization state upon reflection. The configurations of particular interest for current speed and accuracy requirements are the PCSA and PSCA ellipsometers using a monoplate compensator as the rotating element. Among other advantages this allows the polarizer and analyzer to remain in a fixed position during operation, so systematic errors due to e.g. partially polarized light
sources or polarization-sensitive detectors will not arise. In addition, single-element components such as the monoplate compensator are easier to fabricate to minimal beam-deflection specifications, as well as being easier to fabricate and calibrate.

Here I analyze the effect of axial misalignment on the components of the PSCA ellipsometer, obtaining analytical solutions to 1st order. I show that system errors can be separated from the sample or raw machine data analytically. The polarizer and analyzer will be analyzed as well as the monoplate compensator. The monoplate compensator is particularly useful for determining misalignment errors, since these generate sidebands at $1C$, $3C$, and $5C$ where $C$ is the azimuth angle of the monoplate. These are away from the $0C$ (dc), $2C$, and $4C$ components that provide information about the sample, although a particular subset of axial misalignment errors is shown to affect the $2C$ and $4C$ components as well. Sample misalignments will also be considered.

In axially aligned systems the Jones-matrix calculus, which uses only the x- and y-axis projections of the field transmitted through the optical components, is sufficient. Although in the end I will describe misalignment effects on the field components parallel and perpendicular components to the plane of incidence, the calculation itself requires that I take into account the field components projected along the local $z$ axis of the element. In the Jones-matrix approach any misalignments and other abnormalities must be projected into the parallel and perpendicular components of the transmission and reflection coefficients of the system elements, a description that is incomplete. Thus an optical system with misaligned components must be analyzed in all three dimensions. Two of these dimensions will look like a Jones-matrix solution. The third one, the $z$ component, results either from alignment errors or from beams not propagating parallel to the central ray. The procedure that will be developed here is very similar to that which I have used for numerical simulations, except that the effects of axial misalignments are treated to 1st order using Euler rotations. Details will be given below.

Additional comments can also be made. If the source of errors is not known, then systematic errors cannot be separated from sample properties. One can hope to minimize
them during calibration procedures. However, if the mathematical procedures used to extract system parameters from quantities such as the position of the plane of incidence from a minimum of the intensity, for example, assume ideal systems, as is the usual case, then any misalignment will result in improper calibration parameters and will therefore couple to the sample properties resulting in errors. For current accuracy requirements this is unacceptable.

Figure 4-1 shows a PSCA type ellipsometer with possible misalignments. The polarizer, compensator, and analyzer are misaligned mechanically and the incoming beam approaches the surface at an angle different from that of the central ray.

Figure 4-1 Typical misalignments shown for a PSCA ellipsometer. The polarizer, compensator, and analyzer are misaligned mechanically and the incoming beam approaches the surface at an angle different from that of the central ray.
system a short-arc Xe lamp) is focused on the sample, the beams of interest form a cone-shaped distribution of k vectors about the central ray. Ideally the central ray corresponds to the part with the highest intensity, but the source intensity distribution is not necessarily uniform. Being defined mechanically it is easy to relate the central ray, and hence the individual rays of the bundle, to the sample or laboratory frame of reference.

Therefore the first axial misalignment that needs to be considered is the misalignment of the direction of an incoming ray with respect to the central beam. Let the direction of the incoming ray be defined by the angles \((\theta_k, \phi_k)\). Component misalignments are the next that need to be considered, and are defined in that the surface normal of the element is also misaligned with respect to the central beam. Let the direction of the surface normal of a particular element be defined by \((\theta_n, \phi_n)\). Finally, the mechanical rotation axis \(\hat{\omega}\) of the component may also be misaligned relative to the central ray. Let the direction of the rotation axis be defined by \((\theta_\omega, \phi_\omega)\). Of course, ideally the surface normal \(\hat{n}\), mechanical rotation axis \(\hat{\omega}\), wave vector \(k\), and central beam \(\hat{z}\) are all identical, and every ray is parallel to the central beam.

The necessary generalization of the Jones-matrix calculus to 3 dimensions then takes the form

\[
\begin{pmatrix}
E_x^{\text{out}} \\
E_y^{\text{out}} \\
E_z^{\text{out}}
\end{pmatrix} = \begin{pmatrix}
\text{Analyzer} & \text{Compensator} & \text{Sample} & \text{Polarizer}
\end{pmatrix}
\begin{pmatrix}
E_x^{\text{in}} \\
E_y^{\text{in}} \\
E_z^{\text{in}}
\end{pmatrix},
\]

(4.1)

where the matrices indicated symbolically are 3x3 transfer matrices that describe a particular ray field propagating through the PSCA ellipsometer. Unlike 2x2 Jones matrix representations for which the components parallel and perpendicular to the plane of incidence can be used as eigenvectors, here a more complicated representation is necessary. In the next sections I determine the 3x3 matrix for each element and follow the beam through the system.
to obtain the overall system transfer matrix and hence the harmonic spectrum of the reflected beam.

To represent axial misalignments in the central beam coordinate system it is necessary to project or rotate all local coordinates into general laboratory coordinates. Euler rotations are the most general method of doing this. Here we will use such transformations with the assumption that axial misalignments can be treated as small angles so that a 1st order approximation for small rotations can be applied. In order to apply this to our coordinate systems we first define these transformations as arbitrary rotations of coordinates \((\hat{x}, \hat{y}, \hat{z})\) into the \((\hat{x}_1, \hat{y}_1, \hat{z}_1)\) as follows;

i) The first rotation is around the \(\hat{z}\)-axis to bring the \((\hat{x}', \hat{z}, \hat{z}_1)\) axes into the same plane,

\[
\begin{pmatrix}
\hat{x}' \\
\hat{y}' \\
\hat{z}
\end{pmatrix} =
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\hat{x} \\
\hat{y} \\
\hat{z}
\end{pmatrix},
\]  
(4.2)

ii) The second is a polar rotation around the \(\hat{y}'\)-axis to bring \(\hat{z}\)-axis into \(\hat{z}_1\), and

\[
\begin{pmatrix}
\hat{x}'' \\
\hat{y}' \\
\hat{z}_1
\end{pmatrix} =
\begin{pmatrix}
\cos \theta & 0 & -\sin \theta \\
0 & 1 & 0 \\
\sin \theta & 0 & \cos \theta
\end{pmatrix}
\begin{pmatrix}
\hat{x}' \\
\hat{y}' \\
\hat{z}
\end{pmatrix},
\]  
(4.3)

iii) The final is another azimuthal rotation to bring the \(\hat{x}''\)-axis into the \(\hat{x}_1\)-axis.

\[
\begin{pmatrix}
\hat{x}_1 \\
\hat{y}_1 \\
\hat{z}_1
\end{pmatrix} =
\begin{pmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\hat{x}'' \\
\hat{y}' \\
\hat{z}_1
\end{pmatrix},
\]  
(4.4)

This is called the \((\hat{z}, \hat{y}, \hat{z})\) convention [18] and rotations are \((\phi, \theta, \varphi)\). The resulting Euler rotation is written as
Since axial misalignments are generally small they can be represented to 1\textsuperscript{st} order. We assume that both polar and azimuthal rotations are small such that the difference between actual and ideal positions can be taken to 1\textsuperscript{st} order. Then $\theta \approx 0$, azimuthal misalignments are small so that $\phi = -\varphi$, and the last azimuthal rotation brings the azimuth approximately back to its original position. Therefore for small angles Euler rotations can be approximated as

$$R_{\text{Euler}} (\phi, \theta, \varphi) = \begin{pmatrix}
\cos \theta \cos \phi \cos \varphi - \sin \phi \sin \varphi & \cos \theta \sin \phi \cos \varphi - \cos \phi \sin \varphi & -\sin \theta \cos \varphi \\
-\cos \theta \cos \phi \sin \varphi - \sin \phi \cos \varphi & -\cos \theta \sin \phi \sin \varphi + \cos \phi \cos \varphi & \sin \theta \sin \varphi \\
\sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta 
\end{pmatrix}$$

(4.5)

In the next section each of the optical elements is analyzed for its general misalignment condition, with particular emphasis on the monoplate compensator. The polarizer and analyzer will be considered to be ideal, with misalignment resulting only from the incoming beam being off-axis. In fact the results for the monoplate can easily be applied back to the polarizer or analyzer. The sample is analyzed only to describe the effect of wobble caused by substrate rotation.

### 4.1 Polarizer and Analyzer

For simplicity we assume that the polarizer and analyzer are aligned so that the central ray, rotation axis, and surface normal of the surface of interest (the exit face for the polarizer and the entrance face for the analyzer) are parallel. This means that we do not treat potential variations of angles of incidence with azimuth angle, but since our emphasis for polarizing prisms is on beam misalignment we shall discuss axial misalignments only in connection with the monoplate compensator. Here I only show how to represent the polarizer and analyzer as 3x3 field transfer matrices when dealing with off-axis beams. Figure 4-2 is a
schematic diagram of a polarizer, which can also be understood as an analyzer if the beam direction is reversed.

Figure 4-2 Schematic diagram of the polarizer, with the principal axes of the dielectric shown. The beam is misaligned, but no other axial misalignments are assumed.

We start with a general incoming field represented as \( \mathbf{E} = (E_x \hat{x} + E_y \hat{y} + E_z \hat{z}) e^{ikz} \). The propagation vector \( \mathbf{k} \) is assumed to be misaligned only to 1\(^{\text{st}}\) order so that it can be written in central-ray frame using the small term Euler rotation defined in Eq.(4.6) as

\[
\begin{pmatrix}
  k_x \\
  k_y \\
  k_z
\end{pmatrix} =
\begin{pmatrix}
  1 & 0 & -\theta_k \cos \phi_k \\
  0 & 1 & -\theta_k \sin \phi_k \\
  \theta_k \cos \phi_k & \theta_k \sin \phi_k & 1
\end{pmatrix}\begin{pmatrix}
  0 \\
  0 \\
  k_z'
\end{pmatrix}, \tag{4.7}
\]

\[
k = \frac{\omega}{c} (n_x \hat{x} + n_y \hat{y} - 1 \hat{z}). \tag{4.8}
\]

where \( n_x = \theta_n \cos \phi_n \) and \( n_y = \theta_n \sin \phi_n \) are 1\(^{\text{st}}\) order terms. Since the plane of incidence is not yet determined, the only information that we have is that outside of the prism the field is perpendicular to the propagation vector (\( \mathbf{E} \perp \mathbf{k} \)). Therefore z-component of the field can be written in terms of the other two components as \( E_z = n_x E_x + n_y E_y \).
A linear polarizer is designed such that its dielectric tensor is uniaxial with the c-axis of the entrance half lying in the direction of the propagation so that the dielectric tensor of this part is symmetric under rotation.

\[
\tilde{\varepsilon}_1 = \begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_a & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix}.
\] (4.9)

Thus the eigenmodes for propagation for the entrance part are degenerate. It should be noted that if the beam is misaligned the dielectric tensor is not symmetric about the z axis and the modes become nondegenerate. However, this is only a 2\textsuperscript{nd}-order effect and can be neglected.

The second half is designed with the c axis perpendicular to the propagation direction so the eigenmodes are nondegenerate:

\[
\tilde{\varepsilon}_2 = \begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_c & 0 \\
0 & 0 & \varepsilon_a
\end{pmatrix}.
\] (4.10)

The beam of interest is that transmitted through both halves without deflection i.e. the x component of the field with the above dielectric tensor. If the dispersion equation is solved for each half of the polarizer for an off-axis beam, it can be seen that the displacement field of the ordinary beam is

\[
D \propto \begin{pmatrix}
1 \\
0 \\
\frac{n_x}{\sqrt{\varepsilon_a}}
\end{pmatrix},
\] (4.11)

Thus the z-component of the field also contributes to the intensity. Therefore we can write a 3x3 generalization of the 2x2 Jones-matrix equivalent as

\[
\begin{pmatrix}
1 & 0 \\
0 & 0 \\
0 & 0
\end{pmatrix} \Rightarrow \begin{pmatrix}
1 & 0 & n_x \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix},
\] (4.12)
again considering only terms up to 1st order. Rotating the result by the azimuth angle P about
the rotation axis yields the polarizer output, for substitution in the system transfer matrix
Eq.(4.1) as

\[
\begin{pmatrix}
\cos P & 0 & n_x \cos P \\
\sin P & 0 & n_x \sin P \\
n_x & 0 & 0
\end{pmatrix}
\]  

(4.13)

Thus the effect of off-axis transmission through the polarizer is a first-order correction to the
mechanical azimuth angle P. The same results apply to the analyzer prism, since the only
difference is that the beam propagation direction is reversed.

4.2 Substrate

Two aspects must be taken into account when representing the sample in 3x3
transfer-matrix form. First, the angle of incidence varies over the beam if the beam is not
perfectly collimated. For example the beam focusing that we use in all our systems results in
a cone-shaped bundle of rays arriving at the sample. Second, if the substrate is rotated, then
wobble or runout introduces another source of error. Since the effect and treatment of these
errors are different, with wobble being a geometric error that can be corrected by tilt
adjustment and a spread of incidence angles accounted for by integration over the
distribution of wave vectors, for present purposes I will assume for simplicity that wobble
does not occur. In our OMCVD system it appears as a 10ωt component of the transmitted
intensity and will be investigated separately. Hence the procedure that needs to be applied
here is to project the central-ray frame into the sample-normal frame, solve for the s- and p-
polarized components of the reflected wave, and project this wave back into the central-ray
frame of the reflected beam. These operations are again described in 3 dimensions, resulting
in a 3x3 sample matrix.

The sample normal along with the wave vector of the incoming beam defines the
plane of incidence and thus the projections of the incoming field vector onto components
perpendicular and parallel to the plane of incidence, the s- and p-polarized waves. The
directions of the electric fields of these s- and p-polarized components are \((\hat{n}_{\text{sample}} \times \mathbf{k})\) and
\(\mathbf{k} \times (\hat{n}_{\text{sample}} \times \mathbf{k})\). With the \(\mathbf{k}\) defined in the sample-normal frame as below, the s- and p-
polarized components can be written,

\[
\mathbf{k} = \frac{\omega}{c} \left( \hat{x} (\sin \theta_{\text{AOI}} + n_x \cos \theta_{\text{AOI}}) + \hat{y} n_y + \hat{z} (-\cos \theta_{\text{AOI}} + n_x \sin \theta_{\text{AOI}}) \right), \tag{4.14}
\]

\[
\left( \hat{n} \times \hat{k} \right) = \frac{1}{\sin \theta_{\text{AOI}}} \left\{ \hat{x} (-n_x \cos \theta_{\text{AOI}}) + \hat{y} (\sin \theta_{\text{AOI}} + n_x \cos \theta_{\text{AOI}}) + \hat{z} n_y \sin \theta_{\text{AOI}} \right\}, \tag{4.15}
\]

\[
\hat{k} \times (\hat{n} \times \hat{k}) = \frac{1}{\sin \theta_{\text{AOI}}} \left\{ \hat{x} (\sin \theta_{\text{AOI}} + n_x \cos \theta_{\text{AOI}}) + \hat{y} (n_y \cos \theta_{\text{AOI}}) + \hat{z} n_x \cos \theta_{\text{AOI}} \right\}. \tag{4.16}
\]

Therefore the beam arriving the polarizer discussed in the previous section can be
decomposed into perpendicular and parallel component as

\[
E_1 = E \cdot \left( \hat{n} \times \hat{k} \right) \left[ \hat{n} \times \hat{k} \right], \tag{4.17}
\]

\[
E_2 = E \cdot \left( \hat{k} \times (\hat{n} \times \hat{k}) \right) \left[ \hat{k} \times (\hat{n} \times \hat{k}) \right]. \tag{4.18}
\]

As a result the reflected wave will be the combination of incoming waves multiplied
by the reflective coefficients:

\[
\begin{pmatrix}
E_2^{\text{out}} \\
E_1^{\text{out}}
\end{pmatrix} =
\begin{pmatrix}
r_p & 0 \\
0 & r_s
\end{pmatrix}
\begin{pmatrix}
E_2^{\text{in}} \\
E_1^{\text{in}}
\end{pmatrix}. \tag{4.19}
\]

Now projecting into the central-ray frame of the reflected beam we find the 3x3 system transfer
matrix for a slightly misaligned incoming beam to be
When the beam is parallel to the lab frame that is when $n_x = n_y = 0$ then the sample 3x3 matrix reduces to the standard Jones-matrix representation as

$$
\begin{pmatrix}
    r_p & 0 & 0 \\
    0 & r_s & 0 \\
    0 & 0 & 0
\end{pmatrix}.
$$

(4.21)

### 4.3 Monoplate Compensator

**Axially Misaligned Case**

In a PSCA (or PCSA) type ellipsometer, the most important component is the compensator, since it generates the harmonics of the transmitted intensity that are analyzed for the properties of the sample and misalignment parameters of the system. As a result the compensator needs to be investigated thoroughly. In particular, the type of compensator used in our system, the monoplate, has not been investigated previously except for our preliminary report [20]. In this report we showed numerically that misalignment generates $1\omega$, $3\omega$, and $5\omega$ coefficients of the mechanical rotation frequency. However, an analytical solution has not yet determined the extent to which the even coefficients are affected.

In the ideal case the incoming wave vector, rotation axis, surface normal vector, and central ray are all parallel to the local z axis and the incoming electric field has components only in the x and y directions. However, in the general case none of these vectors is parallel. We discuss the general case, showing in Figure 4-3 the definitions of the different angles used below. It is clear that a complete treatment of the monoplate will require a number of coordinate transformations, including those to express the dielectric tensor in the crystal
frame for propagation purpuses and the electric fields in the surface-normal frame to take into account the boundary conditions.

The first step is to express the dielectric tensor in the surface normal frame to obtain the dispersion equation. We use the Euler angles for this purpose. Referring to Figure 4-3, $\theta_c, \phi_c$ are the polar and azimuth angles chosen with respect to the $\hat{n}$ frame. The polar angle is actually determined when the plate is manuactured. The azimuth angle is relative to the zero azimuth of the surface-normal, $\hat{n}$, frame. In principle this can be chosen arbitrarily, but since we are using fields parallel to the plane of incidence in our PSCA ellipsometer we
define this relative to the ordinary ("fast") axis in the reference plane that is formed with central beam axis and surface normal. Because the angle between the surface normal and rotation axis is fixed, it does not affect the overall offset of the compensator angle.

With the rotations defined, we can write the dielectric tensor in terms of the zero and first-order parts as

\[
\tilde{\varepsilon} = \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_c \end{pmatrix} = \begin{pmatrix} \varepsilon + \Delta \varepsilon & 0 & 0 \\ 0 & \varepsilon + \Delta \varepsilon & 0 \\ 0 & 0 & \varepsilon - \Delta \varepsilon \end{pmatrix} = \varepsilon + \Delta \varepsilon \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{4.22}
\]

where \( \varepsilon = (\varepsilon_a + \varepsilon_c)/2 \) and \( \Delta \varepsilon = (\varepsilon_a - \varepsilon_c)/2 \). We rotate this into the \( \hat{n} \) frame using Eq. (4.5).

\[
\tilde{\varepsilon}_n = \varepsilon \tilde{\mathbf{I}} + \Delta \varepsilon \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} R_{\text{Euler}} (\theta_c, \phi_c) \end{pmatrix}^{-1}, \tag{4.23}
\]

\[
\tilde{\varepsilon}_n = \varepsilon \tilde{\mathbf{I}} + \Delta \varepsilon \begin{pmatrix} 1 - 2 \cos^2 \phi_c \sin^2 \theta_c & \sin 2 \phi_c \sin^2 \theta_c & \cos \phi_c \sin 2 \theta_c \\ \sin 2 \phi_c \sin^2 \theta_c & 1 - 2 \sin^2 \phi_c \sin^2 \theta_c & -\sin \phi_c \sin 2 \theta_c \\ \cos \phi_c \sin 2 \theta_c & -\sin \phi_c \sin 2 \theta_c & -\cos 2 \theta_c \end{pmatrix}. \tag{4.24}
\]

The azimuth angle \( \phi_c \) can be assumed to be as 90°. This brings the ordinary (fast) axis into the reference x-z plane, consistent with the relative retardation being positive, and since the surface normal rotates with the plate this is still acceptable. The resulting dielectric tensor in the surface normal frame is

\[
\tilde{\varepsilon}_n = \varepsilon \tilde{\mathbf{I}} + \Delta \varepsilon \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos 2 \theta_c & -\sin 2 \theta_c \\ 0 & -\sin 2 \theta_c & -\cos 2 \theta_c \end{pmatrix} = \begin{pmatrix} \varepsilon + \Delta \varepsilon & 0 & 0 \\ 0 & \varepsilon + \Delta \varepsilon \cos 2 \theta_c & -\Delta \varepsilon \sin 2 \theta_c \\ 0 & -\Delta \varepsilon \sin 2 \theta_c & \varepsilon - \Delta \varepsilon \cos 2 \theta_c \end{pmatrix}. \tag{4.26}
\]
The second part of the problem is to express the propagation vector and \( \mathbf{E} \) fields of the misaligned plate in the \( \hat{n} \) frame where dispersion equation is to be solved. This is accomplished by successive rotations first into the \( \hat{\omega} \) frame, then into \( \hat{n} \) frame. The misalignments can be separated here as beam misalignment, i.e., the beam not propagating parallel to the reference axis, and axial misalignment, i.e., the rotation axis not parallel to the reference axis. For a misaligned beam we can write the propagation and field vectors in terms of the azimuth and polar angles already defined as

\[
\mathbf{k} = \frac{\omega}{c} (\hat{x} \sin \theta \cos \phi + \hat{y} \sin \theta \sin \phi - \hat{z} \cos \theta)
\]

\[= \frac{\omega}{c} (\hat{x} \theta \cos \phi + \hat{y} \theta \sin \phi - \hat{z} \theta)
\]

\[= \frac{\omega}{c} (n_x \hat{x} + n_y \hat{y} - \hat{z})
\]

At this point it is not necessary to know the location of the plane of incidence. The only requirement at present is that \( \mathbf{E} \cdot \mathbf{k} = 0 \). Therefore the field in the laboratory frame can be written as

\[
\mathbf{E} = \begin{pmatrix}
E_x \\
E_y \\
E_z
\end{pmatrix} = \begin{pmatrix}
E_x \\
E_y \\
n_x E_x + n_y E_y
\end{pmatrix}.
\]

The boundary conditions apply in the surface normal frame. Hence the next step is to write the wave and propagation vectors in this coordinate system. Referring to Figure 4-3, the first rotation brings the vectors in to the \( \hat{\omega} \) frame, then mechanical rotation takes place in \( \hat{\omega} \) frame, and finally the vectors are projected into the \( \hat{n} \) frame to yield the components that need to go into the boundary conditions. Again using first-order quantities the operations can be written as
Transmission coefficients and normal modes can now be determined, since we now have the tangential field and propagation vector components entering the monoplate. Again we start with a general wave vector as in Eq. (4.28). Using Eq. (4.29) we now write the propagation vector arriving vector at the surface as

\[
\hat{R}(\hat{\omega}, C, \hat{n}) = \begin{pmatrix}
\cos C & -\sin C & -(\theta_n \cos (C - \phi_n) + \theta_n \cos \phi_n) \\
\sin C & \cos C & -(\theta_n \sin (C - \phi_n) + \theta_n \sin \phi_n) \\
\theta_n \cos \phi_n + \theta_n \cos (C - \phi_n) & \theta_n \sin \phi_n + \theta_n \sin (C - \phi_n) & 1
\end{pmatrix}
\]

(4.29)

The dispersion equation can now be solved using the dielectric tensor in Eq. (4.26). The z component of the propagation vector and therefore indices of refraction for the ordinary and extraordinary modes can be determined and we find

\[
n_o = \sqrt{\varepsilon_{xx}} = \sqrt{\varepsilon_a},
\]

\[
n_e = \sqrt{\varepsilon_{yy} - n_y^2 \frac{\varepsilon_{zz}}{\varepsilon_{zz}}} = \sqrt{\varepsilon + \Delta \varepsilon \cos 2\theta_c - \left(\frac{\Delta \varepsilon \sin 2\theta_c}{\varepsilon - \Delta \varepsilon \cos 2\theta_c}\right)^2} + n'_y \frac{\Delta \varepsilon \sin 2\theta_c}{\varepsilon - \Delta \varepsilon \cos 2\theta_c}.
\]

(4.31)
Clearly, only the extraordinary beam is affected by misalignment to 1st order. For simplicity for further calculation $n_e$ is used to represent as both 0th and 1st order quantities since in a first-order calculation all higher order terms can be neglected. Hence the fields propagated and back-reflected as ordinary and extraordinary modes in the monoplate can be written respectively as

$$
E_o \propto \begin{pmatrix}
(n_e^2 - n_o^2) \varepsilon_{zz} \pm 2n'_y \varepsilon_{yz} n_o \\
\mp n'_x \varepsilon_{yz} n_o \\
\pm n'_z \left( \varepsilon_{yy} - \varepsilon_{xx} \right) n_o
\end{pmatrix}
$$

(4.32)

$$
E_e \propto \begin{pmatrix}
\pm n'_x \varepsilon_{yz} n_e \\
(n_e^2 - n_o^2) \varepsilon_{zz} \pm 2n'_y \varepsilon_{yz} n_e \\
-\left(n_e^2 - n_o^2 \right) \varepsilon_{yz} \pm n'_y n_e \left(n_e^2 - n_o^2 \right) - 2 \left( \varepsilon_{yz}^2 / \varepsilon_{zz} \right)
\end{pmatrix}
$$

(4.33)
The effect of the monoplate on the fields can therefore be written as a 3x3 transmission matrix as

\[
\begin{pmatrix}
E_x^{\text{out}} \\
E_y^{\text{out}} \\
E_z^{\text{out}}
\end{pmatrix}_{\hat{n}-\text{frame}} =
\begin{pmatrix}
t_{11} & t_{12} & n'_x t_{11} \\
t_{12} & t_{22} & n'_y t_{22} \\
n'_x t_{11} & n'_y t_{22} & 0
\end{pmatrix}
\begin{pmatrix}
E_x^{\text{in}} \\
E_y^{\text{in}} \\
E_z^{\text{in}}
\end{pmatrix}_{\hat{n}-\text{frame}}
\]

where z-component defined as in Eq.(4.28). The transmission-matrix elements themselves are determined by the boundary conditions on tangential components of \( \mathbf{E} \) and \( \mathbf{H} \). In terms of the 4x4 transfer matrix \( \mathbf{M} \) for the monoplate, transmission coefficients can be written

\[
t_{11} = \frac{M_{11}}{M_{11}M_{33}} = \frac{1}{M_{33}}, \quad t_{22} = \frac{M_{33}}{M_{11}M_{33}} = \frac{1}{M_{11}}, \quad t_{12} = t_{21} = \frac{-M_{13}}{M_{11}M_{33}},
\]

Figure 4-4 Ordinary and extraordinary index of refraction of MgF\(_2\) is shown.
where coefficients of the 4x4 matrix $M$ are

$$M_{11} = \frac{1}{2n_e} \left\{ e^{-i k_d} \left( 1 + n_e \right)^2 - e^{i k_d} \left( 1 - n_e \right)^2 \right\}, \quad (4.36)$$

$$M_{33} = \frac{1}{2n_o} \left\{ e^{-i k_d} \left( 1 + n_o \right)^2 - e^{i k_d} \left( 1 - n_o \right)^2 \right\}, \quad (4.37)$$

$$M_{13} = \frac{1}{2} \left( -n_e' e_{zz} n_o \right) \left\{ e^{i k_d} \left( \frac{1}{n_e} - 1 \right) \left( n_o - \frac{n_e}{n_o} \right) - e^{-i k_d} \left( \frac{1}{n_o} + 1 \right) \left( n_o + \frac{n_e}{n_o} \right) \right\} \left\{ e^{i k_d} \left( 1 - n_o \right)^2 + e^{-i k_d} \left( 1 + n_o \right)^2 \right\}. \quad (4.38)$$

Using Eqs.(4.35) and ignoring the rapidly oscillating terms on the grounds that the dispersion of our system does not have sufficient wavelength resolution, and also common factors on the basis that our coefficients are normalized, the transmission coefficients can finally be written as

$$t_{11} = \frac{2n_o e^{i k_d}}{\left( 1 + n_o \right)^2}, \quad t_{22} = \frac{2n_e e^{i k_d}}{\left( 1 + n_e \right)^2}, \quad (4.39)$$

$$t_{12} = \frac{1}{2} \left( \frac{n_e' e_{zz} n_o}{n_e^2 - n_e^2} \right) \left\{ e^{i k_d} \left( \frac{1}{n_e} + 1 \right) \left( n_o + \frac{n_e}{n_o} \right) - e^{-i k_d} \left( 1 + n_o \right)^2 \right\} \left\{ \frac{2n_o}{\left( 1 + n_o \right)^2} \frac{2n_e}{\left( 1 + n_e \right)^2} \right\}. \quad (4.40)$$

As a result the system transfer matrix for the monoplate compensator in the central-ray frame becomes

$$T_{mon} = \tilde{T} \left( \hat{\omega}, C, \hat{n} \right) \left( \begin{array}{ccc} t_{11} & t_{12} & n_e' t_{11} \\ t_{12} & t_{22} & n_e' t_{22} \\ n_e' t_{11} & n_e' t_{22} & 0 \end{array} \right) \tilde{T}^{-1} \left( \hat{\omega}, C, \hat{n} \right), \quad (4.41)$$
\[
T_{\text{mon}} = \begin{pmatrix}
\frac{1}{2}(t_{11} + t_{22}) + \frac{1}{2}(t_{11} - t_{22})\cos 2C - t_{12}\sin 2C & \frac{1}{2}(t_{11} - t_{22})\sin 2C + t_{12}\cos 2C & t_{1\eta_x}\cos C - t_{2\eta_y}\sin C \\
\frac{1}{2}(t_{11} - t_{22})\sin 2C + t_{12}\cos 2C & \frac{1}{2}(t_{11} + t_{22}) - \frac{1}{2}(t_{11} - t_{22})\cos 2C + t_{12}\sin 2C & t_{2\eta_x}\cos C + t_{1\eta_y}\sin C \\
t_{1\eta_x}\cos C - t_{2\eta_y}\sin C & t_{2\eta_x}\cos C + t_{1\eta_y}\sin C & 0
\end{pmatrix}
\]

(4.42)

where \( \eta_x = n_x \cos C - n_y \sin C \) and \( \eta_y = -n_x \sin C + n_y \cos C \).

With all the information from polarizer, analyzer, sample and compensator in hand, data from either PSCA or PCSA systems can be analyzed in detail and possible system artifacts and errors can be detected and eliminated, thereby leaving sample properties free from these effects.

We discuss here application to a typical PSCA type ellipsometer showing how these misalignments affect the calibration and therefore the results. To do this we use the 3x3 matrix formulation to calculate the intensity and use it to derive the Fourier coefficients. As mentioned above for PSCA and PCSA ellipsometers the \( dc, 2\omega t \), and \( 4\omega t \) coefficients contain the information about the sample and the \( 10\omega t \) coefficients about surface anisotropy. We deal here with the odd coefficients \( 1\omega t, 3\omega t \), and \( 5\omega t \), in particular focusing on an analytic solution.

During initial calibration the polarizer and analyzer azimuth angles are set at either \( P = 90^\circ, A = 0^\circ \) or \( P = 0^\circ, A = 0^\circ \). Under these conditions sample properties are irrelevant so the reflection coefficients can be set equal to 1 (the reflection matrix becomes the identity matrix). Hence for \( P = 90^\circ, A = 0^\circ \) the intensity in 3x3 matrix form can be written
\[
\begin{pmatrix}
E_{x}^{\text{out}} \\
E_{y}^{\text{out}} \\
E_{z}^{\text{out}}
\end{pmatrix} = \begin{pmatrix}
1 & 0 & n_x \\
0 & 0 & 0 \\
n_x & 0 & 0
\end{pmatrix} \begin{pmatrix}
T_{11} & T_{12} & T_{13} \\
T_{21} & T_{22} & T_{23} \\
T_{31} & T_{32} & 0
\end{pmatrix} \mathbf{x}
\]

\[
\begin{pmatrix} 1 - n_x (\cos^2 \theta_{AOI} - 2) \cos^2 \theta_{AOI} \cot \theta_{AOI} & 0 & n_x (1 - 2 \cos^2 \theta_{AOI} + 2 \cos^4 \theta_{AOI}) \\ 0 & 1 + 2n_x \cot \theta_{AOI} & n_y \\ n_x (1 - 2 \cos^2 \theta_{AOI} + 2 \cos^4 \theta_{AOI}) & n_y & -2n_x \sin \theta_{AOI} \cos^3 \theta_{AOI} \end{pmatrix} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ n_x & 0 & 0 \end{pmatrix}
\]

(4.43)

The resulting wave contains 1st order terms as

\[
\begin{pmatrix} E_{x}^{\text{out}} \\ E_{y}^{\text{out}} \\ E_{z}^{\text{out}} \end{pmatrix} = E_{y}^{\text{in}} T_{12} \begin{pmatrix} 1 + 2n_x \cot \theta_{AOI} \\ 0 \\ n_x \end{pmatrix}.
\]

(4.44)

Intensity is therefore

\[
I \cong |E_{y}^{\text{in}}|^2 |T_{12}|^2 \left\{ 1 + 4n_x \cot \theta_{AOI} \right\},
\]

(4.45)

where \( n_x = \theta_k \cos \phi_k \). The derivation can be taken further if desired by integrating over the distribution of wave vectors making up the complete beam with an appropriate weighting function according to.

\[
I = \iint I(\theta_k, \phi_k) W(\theta_k, \phi_k) \, d^2 r.
\]

(4.46)

This mainly impacts on the normalization of the Fourier coefficients, so it will have a negligible effect on the coefficients.

However the term \( T_{12} \) also contains beam misalignment terms and also will affect the Fourier coefficients. Using Eqs.(4.35) - (4.40), \( |T_{12}|^2 \), the term in which we are interested, can be written
\[
|T_{12}|^2 = |t_{12}|^2 + \frac{1}{4}|t_{11} + t_{22}|^2 \sin^2 2C - \text{Re}\left[ t_{12}^* (t_{11} + t_{22}) \right] \sin 2C. \tag{4.47}
\]

For an ideal and perfectly aligned PSCA (or PCSA) ellipsometer under crossed polarizer operation (either \( P = 90^\circ, A = 0^\circ \) or \( P = 0^\circ, A = 90^\circ \)), the only coefficients that survive are the dc term and \( \cos 4C \), which have equal magnitudes. However Eq.(4.47) shows that when misalignment parameters are introduced to the system transfer function, the term \( \text{Re}\left( t_{12}^* (t_{11} + t_{22}) \right) \) produces sidebands to the \( 2\omega t \) coefficients that have the dependences \( 1\omega t \) and \( 3\omega t \).

\[
\text{Re}\left[ t_{12}^* (t_{11} + t_{22}) \right] = \frac{1}{4} \left( -n'_x e_{xx} n'_o \right) \left[ \frac{1}{2} \left( 1 + n_x' \right) \left( \frac{n_x + n_z}{n_e} \frac{n_x + n_y}{n_o} \right) - \left( 1 + n_o^2 \right) \right] \cos \left( (k_e - k_o) d \right) \quad (4.48)
\]

where \( n'_x = (n_x + \theta_{ox} \cos \phi_{ox}) \cos C - (n_y + \theta_{oy} \sin \phi_{oy}) \sin C + \theta_n \cos \phi_{no} \). Here \( n_x \) and \( n_y \) are the beam misalignment contributions to the Fourier coefficients, with the subscripts \( n \) and \( \omega \) referring to the contributions from surface-normal and rotation-axis misalignments respectively.

By substituting Eq.(4.48) into the Eq.(4.47), it can be seen that misalignments produce not only sidebands but also \( 2\omega t \) coefficients that affect the \( \sin 2C \) contribution as well, the misalignment term carried by the index of refraction of the extraordinary beam also contributes in first order to the \( 2\omega t \) and \( 4\omega t \) coefficients, because retardation is a multiplier of each Fourier coefficient. It is not the electric field but rather the displacement vectors of the ordinary and extraordinary modes that are orthogonal to each other, and since only one of these refractive indices is affected by misalignment the two two modes couple through compensator rotation.

Calibration procedure gives a detail view of where these artifacts in the instrumentation result from and therefore a way to eliminate them. However generally these
results, where calibration configurations are $P = 0^\circ, A = 0^\circ$ or $P = 0^\circ, A = 90^\circ$, are not
linear with experimental configuration (generally used in this work as $P = \pm 30^\circ, A = \pm 30^\circ$). That means these artifacts affecting the sample data cannot simply be eliminated by subtracting calibration result from raw sample data. Therefore misalignment parameters determined in the calibration routine must be applied in a model calculation of the general system transfer matrix for experimental configuration.

The results of this section will also be compared quantitatively to experiment via numerical calculations in Sec. 5.1.2 below.
Chapter 5

5 APPLICATION TO EXPERIMENT

5.1 RCE

5.1.1 System Calibration

In this section, I will briefly explain the calibration procedure of the RC/RS-PSCA ellipsometer that is integrated to the OMCVD reactor as an in-situ probe to monitor real-time growth and control of epitaxial processes. The procedure is relatively complicated, yet is necessary because the accuracy of the data depend on it. The initial discussion involves ideal Jones matrices for each optical element, and thus yields calibration parameters to zero order. First-order corrections are discussed in the following sections. The light beam is assumed to be collimated and all elements axially aligned with the direction of propagation. The first task is to correlate the pixel numbers to the wavelength. For this purpose we use a Hg/Ar light source, comparing the characteristic peaks against pixel number of the photo diode array. Figure 5-1 shows the intensity spectra of such Hg/Ar lamp plotted against pixel number as shown in Fig. 5.4. A simple polynomial fit then relates pixel number to wavelength, and therefore energy.

Calibration routine of a PSCA ellipsometer with monoplate compensator is actually a complicated procedure. How precise your instrument and hence how accurate your data depend on your calibration routine. Therefore here ideal Jones-matrix equations are used for calibration
of each optical element and this yields calibration parameters up to zero order and misalignments can be treated as first order which is discussed in next sections. Light source is assumed to be single beam and parallel to the surface normal of each element. First calibration is to correlate the pixel numbers to the wavelength or energy. A Hg/Ar light source is used for reference spectra and characteristic peaks are compared against each pixel number of the photo diode array. Figure 5-1 shows the intensity spectra of such Hg/Ar lamp plotted against photo diode array pixel numbers. A simple polynomial fit gives the relation between pixel numbers to the energy or wavelength (Figure 5-2).

Figure 5-1 Measured spectrum of Hg/Ar reference lamp plotted against pixel number.
From the ideal Jones-matrix formulation for the ideal system it is seen that for operation of the PSCA ellipsometer at $P = A = 0^\circ$ or $P = 90^\circ, A = 0^\circ$ the sample reflectances are common factors and hence cancel, so the sample acts as a mirror only. Equations (2.63) - (2.69) for the $2\alpha t$ and $4\alpha t$ coefficients provide the basis for the following analysis. We note that for an aligned system $\beta_4/\alpha_4$ goes to zero for $P = 0^\circ$, so minimizing the $\beta_4/\alpha_4$ ratio with respect to $P$ allows us to determine the reference polarizer azimuth corresponding to the condition where the true $P = 0^\circ$.
To determine the analyzer reference azimuth the compensator is removed and the analyzer azimuth adjusted for minimum transmitted intensity. This corresponds to the crossed-polarizer condition, and hence gives the analyzer offset. The reference azimuth of the compensator is then found the fact that $\beta_i$ is zero for $C = 0$. The compensator is further aligned axially by minimizing the odd coefficients, which is done in real time while observing the $1\omega$ and $3\omega$ coefficients on a display screen. Finally, sample runout is minimized with the help of a HeNe laser beam reflected from its surface and projected onto the floor. By adjusting the tilt micrometers of the spindle, the pattern can be reduced to a spot, thereby eliminating sample wobble. Details of these calibration routines, as well as methods of eliminating errors due to higher-order diffraction from the grating, optical activity in the quartz Rochon prisms, etc. can be found in Ref. [5].

These procedures are acceptable for entry-level alignment, but more detailed procedures are necessary to yield the highest accuracy. This is particularly true with the monoplate compensator, which for imperfectly aligned systems requires additional corrections to the data. These can be done in first order as described below.

5.1.2 Determination of Misaligned Parameters – Numerical Solution

In this section, monoplate compensator will be examined and model calculations and simulation will be presented and compared with the experimental data, therefore concluding advantages over other compensator types.

As noted above, the dispersion matrix for the misaligned monoplate yields a quartic dispersion equation instead of the quadratic form as in the Berek plate. Fortunately, since the objective is to eliminate misalignments, a first-order treatment of the effect of misalignments is sufficient for most purposes. As shown in Figure 5-3, there are two types of misalignments that need to be considered: first, the unit surface normal vector $\hat{n}$ is slightly misaligned from the the rotation axis $\hat{\omega}$, and second, the entering wave vector $\hat{k}$ is also slightly misaligned
from $\hat{\omega}$. Therefore the 4x4 matrix method described in the previous section is best suited to evaluate the properties of the misaligned monoplate.

![Diagram](image)

**Figure 5-3** Diagram defining the polar and azimuth angles. The laboratory frame is referenced to the plane of incidence containing the wave vector $\hat{k}$. The rotating axis, surface normal, and c-axis of the birefringent material are represented by $\hat{\omega}$, $\hat{n}$, and $\hat{c}$, respectively. In the ideal case $\hat{k}$, $\hat{\omega}$, and $\hat{n}$ are parallel.

For the case of a misaligned monoplate the situation is more complicated. Defining all the azimuth angles relative to the plane of incidence, the azimuth angles used in the following treatment are defined in Figure 5-3. The laboratory frame is referenced to the plane of incidence containing the wave vector $\hat{k}$. The rotating axis, surface normal, and c-axis of the birefringent material are represented by $\hat{\omega}$, $\hat{n}$, and $\hat{c}$, respectively. Experimental results done with a rotating compensator-PCS A type ellipsometer show that misalignment of monoplate generates $1\omega t$, $3\omega t$, $5\omega t$ coefficients in addition to the usual $2\omega t$, $4\omega t$ coefficients that carry the sample information where $\omega$ is the (mechanical) angular velocity of the plate. However, the extent to which the even coefficients are affected has not yet been established.
The first steps in analyzing the monoplate are to establish suitable reference axes for the laboratory and the monoplate, define their relationship to each other, and describe the misalignments relative to these coordinate systems. We use transformations among three frames of reference, specifically from the internal axes of the plate to its surface normal (a polar rotation by \( \theta_n \)) from the surface normal to the rotation axis \( \hat{\omega} (\theta_n, \phi_n) \) (involving a polar rotation \( \theta_n \) and a azimuthal rotation \( \phi_n \)), and from the rotation frame to the laboratory coordinates \((\theta_n, \phi_n)\). Although the angle of incidence with respect to the surface normal is zero, when \( \hat{n}, \hat{\omega} \) and \( \hat{z} \) are not parallel to each other the angle of incidence becomes coupled to the rotation of the monoplate due to compensator wobble from off-axis rotation.

Starting with the representation of the dielectric tensor of the monoplate in the crystal frame,

\[
\tilde{\varepsilon} = \begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_a & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix},
\] (5.1)

the first rotation establishes the internal tilt angle relative to the surface normal as in Eq.(5.2).

We obtain

\[
\tilde{\varepsilon}' = \begin{pmatrix}
\cos \theta_c & 0 & -\sin \theta_c \\
0 & 1 & 0 \\
\sin \theta_c & 0 & \cos \theta_c
\end{pmatrix}\begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_a & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix}\begin{pmatrix}
\cos \theta_c & 0 & \sin \theta_c \\
0 & 1 & 0 \\
-\sin \theta_c & 0 & \cos \theta_c
\end{pmatrix}.
\] (5.2)

The next transformation takes the above result from \( \hat{n} \) to \( \hat{\omega} \). We use the Euler angles approach [19]. Here all the general method for transformation of crystal axes and coordinate systems. All azimuth angles are referenced to the x-z plane of incidence. Because of rotational symmetry, rotation about the y axis is then sufficient to align the monoplate with the surface normal. Only two angles are needed since the third can be set equal to zero by rotational symmetry. The result is

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\[\tilde{\mathbf{e}}'' = \begin{pmatrix} \cos \theta_n \cos \phi_n & -\sin \phi_n & \sin \theta_n \cos \phi_n \\ \cos \theta_n \sin \phi_n & \cos \phi_n & \sin \theta_n \sin \phi_n \\ -\sin \theta_n & 0 & \cos \theta_n \end{pmatrix} \begin{pmatrix} \cos \theta_n & \cos \phi_n & \sin \theta_n \sin \phi_n & -\sin \theta_n \\ -\sin \phi_n & \cos \phi_n & 0 \\ \sin \theta_n \cos \phi_n & \sin \theta_n \sin \phi_n & \cos \theta_n \end{pmatrix} \]

The last rotation brings the dielectric tensor into the laboratory frame:

\[\tilde{\mathbf{e}}''' = \begin{pmatrix} \cos \theta_{\omega} \cos \phi_{\omega} & -\sin \phi_{\omega} & \sin \theta_{\omega} \cos \phi_{\omega} \\ \cos \theta_{\omega} \sin \phi_{\omega} & \cos \phi_{\omega} & \sin \theta_{\omega} \sin \phi_{\omega} \\ -\sin \theta_{\omega} & 0 & \cos \theta_{\omega} \end{pmatrix} \begin{pmatrix} \cos \theta_{\omega} & \cos \phi_{\omega} & \cos \theta_{\omega} \sin \phi_{\omega} & -\sin \theta_{\omega} \\ -\sin \phi_{\omega} & \cos \phi_{\omega} & 0 \\ \sin \theta_{\omega} \cos \phi_{\omega} & \sin \theta_{\omega} \sin \phi_{\omega} & \cos \theta_{\omega} \end{pmatrix} \]

\[\theta_i = \arccos \left\{ \cos \theta_n \cos \phi_n + \sin \theta_n \sin \phi_n \cos (\phi_n - \phi_{\omega}) \right\} \quad (5.5)\]

Now that we have established the reference coordinates for monoplate, the next step is to put this result into the rotating compensator PCSA configuration as in Figure 5-4Figure 5-4. The system Jones matrix for the PCSA ellipsometer can be written

\[\begin{pmatrix} E_x' \\ E_y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix} \begin{pmatrix} r_p & 0 \\ 0 & r_s \end{pmatrix} \begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix} \begin{pmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} E_x \\ E_y \end{pmatrix} \]

\[ (5.6)\]

where the monoplate is now represented as

\[\begin{pmatrix} t_{11} & t_{12} \\ t_{21} & t_{22} \end{pmatrix} \]

\[ (5.7)\]

Here, \( t_{11}, t_{12}, t_{21}, \text{ and } t_{22} \) are the transmission coefficients defining the transmitted field in terms of the incident components. Since the system is rotationally asymmetrical with respect
to the laboratory frame, rotations must be treated internally using the azimuth angle of rotation $\phi$. Normally the only component used in descriptive of ellipsometer operation are the diagonal elements $t_{11}$ and $t_{22}$, which are usually expressed in further reduced from $t_{11} = 1$ and $t_{22} = e^{i\delta}$, where $\delta$ is the relative retardation. However here we must consider the off-diagonal elements as well including their contribution to the Fourier coefficients.

I next consider experimental verification, which will be done via exact numerical simulations using the 4x4 matrix method to obtain the transmission coefficients and the minors approach described above to eliminate singularities. So that the assessment is quantitative, the hollow-shaft motor carrying the monoplate is mounted on a plate that functions as a geometric clamp allowing adjustment of polar (in plane of incidence) and azimuthal (orthogonal to plane of incidence) angles by two micrometers as shown in Figure 5-4. The laboratory angles are converted into those in the rotation frame according to

$$\phi = \arctan\left(\frac{\sin \phi_x}{\sin \phi_y}\right)$$

$$\theta = \arcsin\left(\sqrt{\sin^2 \phi_x + \sin^2 \phi_y}\right)$$

The analyzer and polarizer angles are set equal to zero so the sample parameters do not affect the results. For this condition and with a perfectly aligned monoplate all odd coefficients and the $\alpha_2$, $\beta_2$ and $\beta_4$ normalized Fourier coefficients should be zero.
The experiment consists of two parts, first to examine the properties of the aligned system, and then to misalign the monoplate deliberately to see whether the observed effect on the Fourier coefficients can be reproduced through the numerical simulation. The sample was a Si wafer. The internal tilt angle of the MgF$_2$ monoplate is 7.660°, which yields a retardation of 90° at a photon energy of 2.915 eV. In particular, the functional dependences of retardation and wavevector projections onto the surface gives rise to sidebands of the dc, 2$\omega t$, and 4$\omega t$ coefficients at $\omega t$, 3$\omega t$, and 5$\omega t$, whose values can be measured and compared to the results of numerical calculations.

I first align the polarizer and analyzer azimuths using the even coefficients as described above. The monoplate is next aligned using the two micrometers. Since the odd Fourier coefficients should vanish for perfect alignment, the procedure basically involves minimizing the $\omega t$, 3$\omega t$, and 5$\omega t$ sine and cosine coefficients. In practice we use the square of the coefficients, since the sine and cosine coefficients do not exactly go to zero together under the same conditions. The resulting coefficients under nearly aligned conditions are shown in Figure 5-5.
I now consider the deliberately misaligned case. The data are shown in Figure 5-6. A computer simulation of the model described above is fitted to these data using as parameters the tilt angle $\theta_c$, compensator phase $\phi_c$, analyzer offset $A$, and misalignment parameters $\theta_a$, $\theta_o$, and $\phi_o$. The analyzer offset and compensator phase angles can be confirmed in both aligned and misaligned case using the even coefficients, as they must go to zero under the selected conditions.
Figure 5-6 Cosine coefficients of the normalized first, third, and fifth Fourier coefficients for an intentionally misaligned monoplate. The theoretical calculations are shown as the dashed lines.

The theoretical results are also shown in Figure 5-5 and Figure 5-6. The spectral dependences of all coefficients are distinctive and are accurately reproduced by the numerical calculations. By comparing these to the data, highly accurate values of the misalignment parameters can be obtained. Results confirm the internal tilt angle of the monoplate as $7.6575^\circ$. The misalignment parameters for Figure 5-5 are $0.0026^\circ$, $0.026^\circ$, and $8.00^\circ$ for $\theta_n$, $\theta_o$, and $\phi_o$, respectively. For Figure 5-6 the corresponding values are $0.0026^\circ$, $0.428^\circ$, and
6.28°. The values of θₙ are identical in both cases, since the mounting of the plate in the hollow shaft is independent of the adjustment of the overall alignment. In Figure 5-7 and Figure 5-8, I compare the $3\omega t$ and $5\omega t$ coefficients for the aligned and misaligned cases, showing that they have the same spectral dependences. [20]

Figure 5-7 Comparison of the $3\omega t$ cos coefficients for nearly aligned and misaligned operation of the monoplate.
Figure 5-8 Comparison of $5\omega t$ coefficients for nearly aligned and misaligned operation of the monoplate.

The sine and cosine terms of all odd coefficients should vanish simultaneously when the monoplate is aligned. However, we observe that the $1\omega t$ and $3\omega t$ coefficients vanish under different conditions, indicating the existence of another mechanism affecting the retardation properties of the plate, possibly stress.

Another important question is to how these misalignments affect the $2\omega t$ and $4\omega t$ coefficients that are used to obtain information about the sample under operating conditions ($P=0^\circ$, $A=-30^\circ$). The results for the normalized $2\omega t$ and $4\omega t$ coefficients for the aligned and
misaligned cases are shown in Figure 5-9. Results are consistent with expectations in that the monoplate misalignments affect the dc, $2\omega t$, and $4\omega t$ terms only to second order.

Figure 5-9 Effect of monoplate misalignment on the normalized sine and cosine $2\omega t$ and $4\omega t$ coefficients under operating conditions with the Si sample.

5.2 RDS – Anisotropy Analysis of the Overlayer Contribution

The sample rotation capability of our integrated RS-RC/PSCA ellipsometer system, allows us to extract information about surface-induced optical anisotropy as well as the
standard ellipsometric information such as dielectric functions and layer thicknesses for materials and structures. However since the system is operated at non-normal incidence, the acquired anisotropy spectra are not the same as those obtained at normal incidence. Furthermore, the signals are much smaller and tend to be highly correlated with other system parameters such as the Fourier coefficients of the transmitted intensity and those obtained by calibration. Because the signals are small, the signal-to-noise ratio of the anisotropy contribution is not as good as that of the $2\cot$ and $4\cot$ coefficients used to obtain the ellipsometric information and misalignment is a bigger factor. Finally, most anisotropy spectra in the literature were obtained at normal incidence, so if we want to make positive identifications of our surface structures and provide our results in a form useful to other workers, it is necessary to relate our non-normal-incidence spectra to their normal incidence equivalents.

The three-layer (substrate/overlayer/ambient) model with a thin anisotropic overlayer is generally a good approximation and can be used to obtain an analytic expression of our non-normal-incidence anisotropy spectra, which in turn can be used to analyze our anisotropy data. We start by defining the overlay dielectric tensor and then determine the equations for the three-phase model with thin anisotropic overlayer. We then adopt the solutions previously obtained by Hingerl et al. [17] to our specific case of a rotating-compensator ellipsometer with a synchronously rotating sample.

In the normal-incidence RDS case, the expression and the spectra are independent of the isotropic part and z-axis projections of the overlayer dielectric function. However in the non-normal incidence case, the overlayer dielectric function must be known if the expression is to be evaluated exactly. However, in our application we can assume to a good approximation, in our application we can assume that the isotropic and z-projected components of the overlayer dielectric function are the same as that of the substrate. With these assumptions the expressions can be evaluated and the equivalent normal-incidence spectra that we obtain is very similar to directly obtained spectra, thereby justifying our approach.
We begin with the general expression for the overlayer dielectric function in the crystallographic frame of reference:

\[
\begin{pmatrix}
\varepsilon_a & 0 & 0 \\
0 & \varepsilon_b & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix}.
\]  

(5.10)

For anisotropy calculations we can also express this in terms of differences:

\[
\begin{pmatrix}
\varepsilon + \Delta\varepsilon & 0 & 0 \\
0 & \varepsilon - \Delta\varepsilon & 0 \\
0 & 0 & \varepsilon_c
\end{pmatrix}
\]  

(5.11)

where \(\Delta\varepsilon = (\varepsilon_a - \varepsilon_b)/2, \ \varepsilon = (\varepsilon_a + \varepsilon_b)/2\). We next suppose that \(d << \lambda\), so we can use the, analytic expressions for \(r_{ss}, r_{pp}, r_{sp}\) and \(r_{pv}\) from K. Hingerl et al.[17] can be used. These are:

\[
r_{pp} = r_{pp}^o \left(1 + \frac{4\pi\text{id} n_{a\perp}}{\lambda (\varepsilon_s - \varepsilon_a)} \varepsilon_s - \varepsilon - (\varepsilon_s / \varepsilon_c - \varepsilon / \varepsilon_s) \varepsilon_a \sin^2 \theta + (\Delta\varepsilon / \varepsilon_s) n_{s\perp}^2 \cos 2\phi \right) \left[\cos^2 \theta - (\varepsilon_a / \varepsilon_s) \sin^2 \theta\right],
\]  

(5.12)

\[
r_{ss} = r_{ss}^o \left(1 + \frac{4\pi\text{id} n_{a\perp}}{\lambda} \varepsilon_s - \varepsilon - \Delta\varepsilon \cos 2\phi \right),
\]  

(5.13)

\[
r_{sp} = -r_{pv}^o \frac{4\pi\text{id} n_{a\perp}}{\lambda} \frac{n_a n_{s\perp} \Delta\varepsilon \sin 2\phi}{(\varepsilon_s n_{a\perp} + \varepsilon_a n_{s\perp})(n_{a\perp} + n_{s\perp})},
\]  

(5.14)

where \(n_{a\perp} = n_a \cos \theta, \ n_{s\perp} = \sqrt{\varepsilon_s - \varepsilon_a \sin^2 \theta}\), \(\Delta\varepsilon\) and \(\varepsilon\) are defined as above, and the reflection coefficients of the bare substrate are given as

\[
r_{ss}^o = \frac{n_{a\perp} - n_{s\perp}}{n_{a\perp} + n_{s\perp}}.
\]  

(5.15)
These anisotropic reflection coefficients can be related to the three-phase model with a thin isotropic layer by assuming that \( \varepsilon = \varepsilon_a \). We can break up the above reflection coefficients into in-plane isotropic and anisotropic parts. For \( r_{pp} \) the expressions are

\[
 r_{pp} = r_{pp}^o \left( 1 + \frac{4\pi i\varepsilon_a}{\lambda (\varepsilon_s - \varepsilon_a)} \varepsilon_s - \varepsilon - \left( \frac{\varepsilon_s}{\varepsilon_s / \varepsilon_a} \right) \varepsilon_s \sin^2 \theta \right) + r_{pp}^o \frac{4\pi i\varepsilon_a}{\lambda (\varepsilon_s - \varepsilon_a)} \frac{\Delta \varepsilon / \varepsilon_a}{[\cos^2 \theta - (\varepsilon_a / \varepsilon_s) \sin^2 \theta]} \cos 2\phi.
\]

or in short

\[
 r_{pp} = r_{pp}^i + r_{pp}^a \cos 2\phi.
\]

The equivalent expressions for \( r_{ss} \) and \( r_{sp} = -r_{ps} \) are

\[
 r_{ss} = r_{ss}^o \left( 1 + \frac{4\pi i\varepsilon_a}{\lambda (\varepsilon_s - \varepsilon_a)} \varepsilon_s - \varepsilon - \left( \frac{\varepsilon_s}{\varepsilon_s / \varepsilon_a} \right) \varepsilon_s \sin^2 \theta \right) - r_{ss}^o \frac{4\pi i\varepsilon_a}{\lambda (\varepsilon_s - \varepsilon_a)} \Delta \varepsilon \cos 2\phi.
\]

or in short

\[
 r_{ss} = r_{ss}^i + r_{ss}^a \cos 2\phi.
\]

\[
 r_{sp} = -r_{ps} = r_{sp}^i \sin 2\phi.
\]

Note that the above does not involve the \( 2\omega_t \) and \( 4\omega_t \) coefficients and hence does not affect our ability to determine the pseudodielectric function from the two-phase model. Therefore the RS-RC/PSCA ellipsometer can be used to evaluate the surface-anisotropy spectra from the \( 10\omega_t \) coefficients.

To obtain the analytical solution for the anisotropy spectra, we start with the Jones matrix representation for the ideal RS-RC/PSCA configuration:
\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} = \begin{pmatrix}
1 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
\cos A & \sin A \\
-sin A & \cos A
\end{pmatrix}
\begin{pmatrix}
\cos C & -\sin C \\
\sin C & \cos C
\end{pmatrix}
\begin{pmatrix}
1 & 0 \\
0 & e^{i\phi}
\end{pmatrix}
\begin{pmatrix}
\cos C & \sin C \\
-sin C & \cos C
\end{pmatrix}
\begin{pmatrix}
0 & 1 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
E'_x \\
E'_y
\end{pmatrix},
\]

(5.22)

\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix} = e^{-i\delta/2}
\begin{pmatrix}
\cos A & \sin A \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
\cos(\delta/2) - i\sin(\delta/2)\cos 2C & -i\sin(\delta/2)\sin 2C \\
-i\sin(\delta/2)\sin C & \cos(\delta/2) + i\sin(\delta/2)\cos 2C
\end{pmatrix}
\begin{pmatrix}
0 & 1 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
E'_x \\
E'_y
\end{pmatrix},
\]

(5.23)

Further simplifications can be made by defining \( r'_p = r_{pp} + r_{ps} \tan P \) and \( r'_s = r_{ss} + r_{sp} \cot P \). Then

\[
\mathbf{E} = \hat{x} \ E_x e^{-i\delta/2}
\begin{pmatrix}
\cos A \left[ r'_p \left( \cos \left( \frac{\delta}{2} \right) - i\sin \left( \frac{\delta}{2} \right) \cos 2C \right) - i r'_s \sin \left( \frac{\delta}{2} \right) \sin 2C \right] + \\
\sin A \left[ -i r'_p \sin \left( \frac{\delta}{2} \right) \sin 2C + r'_s \left( \cos \left( \frac{\delta}{2} \right) + i\sin \left( \frac{\delta}{2} \right) \cos 2C \right) \right]
\end{pmatrix},
\]

(5.24)

where \( r'_p = r'_p \cos P \), and \( r'_s = r'_s \sin P \).

The measured quantity is the intensity, which we can write as a Fourier series with respect to the compensator azimuth angle \( C = \omega t + C_o \):

\[
I = \left| \mathbf{E} \right|^2 = \left\{ d c' + a'_2 \cos 2C + b'_2 \sin 2C + a'_4 \cos 4C + b'_4 \sin 4C \right\},
\]

(5.25)

where the prime denotes that these coefficients have time dependences as a result of sample rotation according to

\[
\phi = \phi_0 + \omega t,
\]

(5.26)
where \( \omega_c \) and \( \omega_s \) are the angular speed of the compensator and sample. The time dependences of the primed coefficients are in addition to those arising from C. Since the sample has \( \pi \) rotation symmetry with respect to \( \phi \), the \( dc \) term will generate a coefficient at \( 2\phi = 2\phi_0 + 2\omega_c t \). The remaining terms will generate sidebands that will obscure the ellipsometric data unless they occur frequencies other than \( 2\omega_t \) and \( 4\omega_t \). This is the reason that we synchronize sample rotation at a 5-to-1 ratio relative to that of the compensator, in which case the anisotropy data appear at \( 10\omega_t \). In this case the anisotropy and ellipsometric contributions are completely independent, so their phases can be determined and information extracted without affecting each other.

The ellipsometric coefficients can be written in final form as

\[
dc' = \frac{|E_s|^2}{2} \left[ \left( |r_p|^2 + |r_s|^2 \right) + \cos^2 \left( \frac{\delta}{2} \right) \left[ \left( |r_p|^2 - |r_s|^2 \right) \cos 2A + 2 \Re(r_p^{*}r_s^*) \sin 2A \right] \right] \quad (5.27)
\]

\[
a'_2 = -|E_s|^2 \sin \delta \Im(r_p^{*}r_s^*) \sin 2A \quad , \quad (5.28)
\]

\[
b'_2 = |E_s|^2 \sin \delta \Im(r_p^{*}r_s^*) \cos 2A \quad , \quad (5.29)
\]

\[
a'_4 = \frac{|E_s|^2}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |r_p|^2 - |r_s|^2 \right) \cos 2A - 2 \Re(r_p^{*}r_s^*) \sin 2A \right] \quad , \quad (5.30)
\]

\[
b'_4 = \frac{|E_s|^2}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |r_p|^2 - |r_s|^2 \right) \sin 2A + 2 \Re(r_p^{*}r_s^*) \cos 2A \right] . \quad (5.31)
\]

With a 5:1 substrate: compensator rotation ratio, \( r_p^{*} \) and \( r_s^{*} \) have \( 0^{th} \) and \( 10^{th} \) harmonic terms. Thus we write the reflection coefficients as

\[
r'_p = r_p^{i} + r_p^{o} \cos 2\phi - r_p^{o} \tan P \sin 2\phi \quad , \quad (5.32)
\]
\[ r_s' = r_s^i + r_{ss}^i \cos 2\phi + r_{sp}^i \cot P \sin 2\phi, \quad (5.33) \]

\[ r_p^\prime = r_{pp}^i \cos P + r_{pp}^o \cos P \cos 2\phi - r_{sp}^o \sin 2\phi, \quad (5.34) \]

\[ r_s^\prime = r_s^i \sin P + r_{ss}^i \sin P \cos 2\phi + r_{sp}^o \cos P \sin 2\phi. \quad (5.35) \]

Substituting these into Eqs.(5.27)-(5.31), we can get all the harmonics that the ideal system produces to first order in the surface anisotropy. Performing the calculations yields

\[
dc = \frac{1}{2} \left[ |r_{pp}|^2 \cos^2 P + |r_{ss}|^2 \sin^2 P \right] \left[ \left( \frac{1}{2} \right) \cos^2 \left( \phi \right) \right] \left[ \left( \frac{1}{2} \right) \cos^2 \left( \phi \right) \right] \left[ \cos 2A \right]
\]

\[
+2 \text{Re} \left( r_{pp}^\prime r_{ss}^\prime \right) \cos P \sin P \sin 2A \right], \quad (5.36) \]

\[
a_{10} = \frac{1}{2} \text{Re} \left( r_{pp}^o r_{pp}^o \cos^2 P + r_{ss}^o r_{ss}^o \sin^2 P \right) \left[ \cos 2A \Re \left( r_{pp}^o + r_{pp}^o \sin 2P \right) \right]
\]

\[
+2 \sin 2A \text{Re} \left( r_{pp}^o r_{ss}^o + r_{ss}^o r_{pp}^o \sin 2P \right), \quad (5.37) \]

\[
b_{10} = -\frac{1}{2} \text{Re} \left( r_{sp}^o \left( r_{pp}^o - r_{ss}^o \right) \right) \sin 2P - \frac{1}{2} \cos^2 \left( \phi \right) \left[ \cos 2A \Re \left( r_{sp}^o \left( r_{pp}^o + r_{pp}^o \right) \right) \right]
\]

\[
+2 \sin 2A \text{Re} \left( r_{sp}^o \left( r_{pp}^o \cos^2 P - r_{ss}^o \sin^2 P \right) \right) \right], \quad (5.38) \]

where the terms are now time independent.

The isotropic parts of \( r_{pp} \) and \( r_{ss} \) can be represented as \( r_{pp}^i = r_{pp}^o \left( 1 + \eta_p \right) \) and \( r_{ss}^i = r_{ss}^o \left( 1 + \eta_s \right) \), where \( \eta_p \) and \( \eta_s \) are first order terms in \( d/\lambda \). These can be calculated if the overlayer dielectric function is extracted, but for our calculation where substrate and overlayer dielectric functions are similar these can be approximated as zero. These terms are

\[
\eta_p = \frac{4\pi i d \nu_{\pm}}{\lambda (\epsilon_s - \epsilon_a)} \left( \frac{\epsilon_s - (\epsilon_s / \epsilon_a) \epsilon_a \sin^2 \theta}{\cos^2 \theta - (\epsilon_a / \epsilon_s) \sin^2 \theta} \right), \quad (5.39) \]
\( \eta_s = \frac{4\pi id\eta_{n\perp}}{\lambda} \frac{\epsilon_s - \epsilon}{\epsilon_s - \epsilon_a} . \) \hspace{1cm} (5.40)

The \( dc \) term can be written to first order as

\[
dc = 2 \left[ \left( |r_{pp}^o|^2 (1 + 2 \text{Re}(\eta_p)) \cos^2 P + |r_{ss}^o|^2 (1 + 2 \text{Re}(\eta_s)) \sin^2 P \right) \\
+ \cos^2 \left( \frac{\delta}{2} \right) \cos 2A \left( |r_{pp}^o|^2 (1 + 2 \text{Re}(\eta_p)) \cos^2 P - |r_{ss}^o|^2 (1 + 2 \text{Re}(\eta_s)) \sin^2 P \right) \right] . \hspace{1cm} (5.41)
\]

Since the \( 10\omega t \) terms are already first order in the anisotropy we only need to evaluate the \( dc \) term to lowest order. However, we give both below:

\[
dc = 2 \left[ |r_{pp}^o|^2 \cos^2 P + |r_{ss}^o|^2 \sin^2 P \right]  + 2 \cos^2 \left( \frac{\delta}{2} \right) \left[ \cos 2A \left( |r_{pp}^o|^2 \cos^2 P - |r_{ss}^o|^2 \sin^2 P \right) \\
+ \sin 2A \text{Re} \left( r_{pp}^o r_{ss}^* \right) \sin 2P \right] \\
+ 4 \left( |r_{pp}^o|^2 \text{Re}(\eta_p) \cos^2 P + |r_{ss}^o|^2 \text{Re}(\eta_s) \sin^2 P \right) \\
+ 2 \cos^2 \left( \frac{\delta}{2} \right) \left[ \cos 2A \left( |r_{pp}^o|^2 \text{Re}(\eta_p) \cos^2 P - |r_{ss}^o|^2 \text{Re}(\eta_s) \sin^2 P \right) \\
+ \sin 2A \text{Re} \left( r_{pp}^o r_{ss}^*(\eta_p^* + \eta_s) \right) \sin 2P \right] . \hspace{1cm} (5.42)
\]

The above equations also define the coefficients of the \( 10^{th} \) harmonics terms to first order for the a RS-RC/PSCA configuration.

We now relate these coefficients to the normal incidence RDS spectra, To do this we use Eqs.(5.17)-(5.21) and express the result this in terms of \( \Delta \tilde{r}/\tilde{r} \). The RDS signal is defined as

\[
\frac{\Delta \tilde{r}}{\tilde{r}} = \frac{8\pi idn_s \Delta \epsilon}{\lambda (\epsilon_s - \epsilon_a)} = \frac{\Delta r}{r} + i \Delta \theta , \hspace{1cm} (5.43)
\]
In principle any angles P and A can be used, but the most favorable configuration is that which gives the best signal-to-noise ratio, ideally for the ellipsometric as well as the $10\omega\xi$ data. The reference phase $\phi_o$ for $\phi$ must also be determined to get correct values of $a_{10}$ and $b_{10}$. Polarizer and analyzer settings of $0^\circ$ and $90^\circ$ are used to accomplish this and to detect any background or nonlinearity that might be present in the system. This will be explained in the next subsection. As mentioned above the $dc$ term can be assumed to be of $0^{th}$ order, that is unaffected by surface anisotropy.

To establish the connections between $\alpha_{10}$, $\beta_{10}$ and normal-incidence RDS spectra, we assume that $\varepsilon = \varepsilon_c$. Thus our expression pertains to a small anisotropy over an isotropic substrate. The result is

$$r_{ss}^a = -\frac{1}{2} r_{ss}^o \left( \frac{\Delta \tilde{r}}{\tilde{r}} \right) \cos \theta,$$

$$r_{pp}^a = \frac{1}{2} r_{pp}^o \left( \frac{\Delta \tilde{r}}{\tilde{r}} \right) \gamma \cos \theta,$$

where for $\varepsilon = \varepsilon_c$

$$\gamma = \frac{\varepsilon_x - \varepsilon_o \sin^2 \theta}{\varepsilon - (\varepsilon_x + \varepsilon_o) \sin^2 \theta}$$

and

$$r_{sp}^a = \frac{1}{2} r_{ss}^o \left( \frac{\Delta \tilde{r}}{\tilde{r}} \right) \zeta,$$

where

$$\zeta = \frac{(\varepsilon_x - \varepsilon_o) n_{a \perp} n_{s \perp}}{(\varepsilon, n_{a \perp} + \varepsilon_o n_{s \perp})(n_{a \perp} - n_{s \perp})}.$$
\[
dc = \frac{1}{4} \left[ \left| \rho \right|^2 + 2 \left( \left| \rho \right|^2 - 1 \right) \cos 2P + 2 \Re \left( \rho \sin 2P \sin 2A \right) \right] \cos^2 \left( \frac{\delta}{2} \right) \left[ \left| \rho \right|^2 - 1 + \left| \rho \right|^2 \cos 2P \cos 2A \right] \cdot 
\]

\[
a_{10} = \frac{1}{4} \left| r_{ss}^0 \right|^2 \cos \theta \left\{ \left[ \left| \rho \right|^2 \Re \left( \gamma \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right) - \Re \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right] + \left[ \left| \rho \right|^2 \Re \left( \gamma \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right) + \Re \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right] \cos 2P \right\} + \cos^2 \left( \frac{\delta}{2} \right) \left\{ \left[ \left| \rho \right|^2 \Re \left( \gamma \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right) + \Re \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right] + \Re \left( \rho^* \gamma^* \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) - \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \right) \sin 2P \sin 2A \right\} \cdot (5.48)
\]

\[
b_{10} = -\frac{1}{4} \left| r_{ss}^0 \right|^2 \cos^2 \left( \frac{\delta}{2} \right) \left\{ \Re \left( \rho^* - 1 \right) \zeta \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \sin 2P + \left[ \Re \left( \rho^* + 1 \right) \zeta \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \sin 2P \cos 2A \right] \right\} \cos \theta \left\{ \Re \left( \rho^* - 1 \right) \zeta \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) + \Re \left( \rho^* + 1 \right) \zeta \left( \frac{\Delta \bar{\rho}}{\bar{\rho}} \right) \cos 2P \right\} \sin 2A \right\} \cdot (5.49)
\]

where \( \rho = \frac{\rho_{pp}}{\rho_{ss}} \).

The above equations can be inverted to obtain the real and imaginary parts of \( \Delta \bar{\rho}/\bar{\rho} \), namely magnitude \( \Delta \bar{\rho}/\bar{\rho} \) and phase \( \Delta \theta \) of the equivalent normal-incidence RDS spectra. The two quantities that are important are \( \varepsilon = (\varepsilon_x + \varepsilon_y)/2 \), and \( \Delta \varepsilon = (\varepsilon_x - \varepsilon_y)/2 \). For normal-incidence only \( \Delta \varepsilon \) is used. However only \( a_{10} \) and not \( b_{10} \) requires the assumption that \( \varepsilon = \varepsilon_x \).
Thus the $b_{10}$ coefficient actually possesses the same advantage of the normal-incidence RD measurement: the measured anisotropy spectrum is independent of $\varepsilon_{s,o}$.

Although RDS and anisotropy information can be deducted from $a_{10}$ and $b_{10}$ themselves, the more usual approach is to normalize these coefficients by dividing them by dc term thus eliminate the scaling factor.

$$\alpha_{10} = \frac{a_{10}}{dc}, \quad (5.50)$$

$$\beta_{10} = \frac{b_{10}}{dc}, \quad (5.51)$$

In the above equations the complex reflectance ratio is technically that of a bare substrate, but for multilayer samples the pseudodielectric function of the sample can be used in place of this to provide for faster data analysis.

Equations (5.50) and (5.51) are the general solution for the normalized 10th harmonic spectra. It is easily seen that $\alpha_{10}$ spectra originate from the anisotropy $(r_{pp} - r_{ss})$ of diagonal elements of the sample Jones matrix, whereas $\beta_{10}$ results from the off-diagonal elements $r_{ps}$ and $r_{sp}$. The connections between RDS spectra and $\alpha_{10}$ and $\beta_{10}$ are general, and do not require any particular values of $P$ and $A$. Therefore $P$ and $A$ values that result in optimum sensitivity for the ellipsometric quantities can be used for anisotropy spectra as well.

In essence, we have shown that a simple numerical conversion routine is sufficient to extract normal-incidence equivalent of our non-normal-incidence anisotropy spectra. Since

$$\begin{pmatrix} \alpha_{10} \\ \beta_{10} \end{pmatrix} = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \begin{pmatrix} \Delta r / r \\ \Delta \theta \end{pmatrix}, \quad (5.52)$$
where matrix $M$ contains coefficients of Eqs.(5.50) and (5.51). Therefore normal-incidence spectra can be calculated as

$$\begin{pmatrix} \frac{\Delta r}{r} \\ \Delta \theta \end{pmatrix} = M^{-1} \begin{pmatrix} \alpha_{10} \\ \beta_{10} \end{pmatrix}.$$  \hspace{1cm} (5.53)

**5.3 Comparison with experiment: Effects of Misalignment**

In this section I present results showing the connection of the $10^{th}$ harmonic coefficients with normal-incidence anisotropy spectra. For this work I use (110)Si, for which the surface-anisotropy spectrum is relatively large (about 1% of the total reflectance) and has been thoroughly studied. [21, 22, 23] For reference purposes the normal-incidence RD spectrum of the sample studied here is given in Figure 5-10.

![Figure 5-10 Normal Incidence RD spectra for Si-110](image-url)
Figure 5-11 shows normalized $10\omega t$ spectra of arbitrary phase taken with the integrated system on the same sample with $P = A = 0^\circ$ and an angle of incidence of $71^\circ$ in the integrated system. These are the P and A settings used for calibrating the sample phase and system artifacts. It is immediately apparent that these data are very similar to normal-incidence spectra except for an offset that appears to be linear in energy. One of the contributing factors to this offset is the time delay in recording the spectra at each pixel, since the sample rotates by approximately $0.05^\circ$ between each pixel measurement.

Figure 5-11. $10\omega t$ spectra taken with the integrated system without any processing.
The analytic solution shows that $\beta_{10}$ is zero for $P = A = 0^\circ$. Although system artifacts are present in the data, these do not contain any spectral features due to the sample. This condition can be used to determine the actual phase of the $10\omega t$ signal. We do this by rotating the $10\omega t$ coefficients into each other by (show equation) so that the spectral dependence due to the sample vanishes in one of the spectra, which can then be assigned to $\beta_{10}$. Figure 5-12 shows the result. In this case the rotation required is $88^\circ$. Note that $\beta_{10}$ still does not vanish completely, but has a background that is linear in energy. This still needs to be subtracted from both $10\omega t$ coefficients.

Figure 5-12. $10\omega t$ spectra of (110)Si after correction by an $88^\circ$ phase offset.
Similar backgrounds are also observed in other coefficients such as $2\omega t$ or $5\omega t$, which also should be zero for $P = A = 0^\circ$. The origin of these linear backgrounds has not been positively identified, but is clearly related to the alignment of the beam entering the spectrometer. Using the appearance of linear backgrounds in these other coefficients as a justification, I perform a least-squares fit of a linear function to the $\beta_{10}$ coefficients and subtract this background from the data. Figure 5-13 shows the result. Therefore these calibration results can be applied to the operation configuration to obtain corrected spectra in order to be used in the conversion routine.

Figure 5-13. Background of the Si(110) $10\omega t$ spectra obtained by least-squares fitting. The solid-line spectra are phase and background corrected.
In Figure 5-14 we compare shows the corrected $10\omega t$ spectra to those calculated using normal-incidence data. The good agreement shows that the theory, the phase calculation, and the background correction are acceptable. The results of the inverse calculation are shown in Figure 5-15. Although the peak fits are reasonable, deviations at lower energies show that other mechanisms may be present to affect the data. This part of the spectral region is particularly sensitive to small changes in quantities.

Figure 5-14. Comparison of corrected $10\omega t$ spectra taken with $P = A = 30^\circ$ and an angle of incidence of $71^\circ$ with those calculated using normal-incidence data.
Unfortunately, not all combinations of $P$ and $A$ result in good normal-incidence equivalents. Because the anisotropy signal is of the order of $10^3$ smaller than that for the dielectric function, the achievable signal-to-noise ratio has a larger effect on the anisotropy data. Figure 5-16 and Figure 5-17 show the data taken at $P = A = 45^\circ$. Again the phase $\Delta \theta$ is the most affected by the configuration of $P$ and $A$. Other configurations have also been investigated although results not put here. It shows that the $P = A = 30^\circ$ configuration gives the best results for both the dielectric function spectra and anisotropy spectra.
Figure 5-16. $10\omega t$ spectra obtained for $P = A = 45^\circ$ together with those simulated from normal-incidence results.
Our general conclusion is that ellipsometers taking data on rotating substrates can also be used to obtain surface-anisotropy spectra that can be correlated to corresponding normal-incidence RD spectra, but care is required in choosing optimal values of P and A. In the non-normal-incidence case the analytic representation suggests that the results depend on $\varepsilon$ as well as on $\Delta\varepsilon$, but our calculations show that the main contribution still originates with $\Delta\varepsilon$, as in the normal-incidence case. In worst-case situations we can always use the values obtained from the even coefficients. However, the coefficient $\beta_{10}$ does not depend on $\varepsilon$ and
hence has no bulk contribution. Consequently, it can be used in exactly the same way as the magnitude $\Delta r/r$ of the corresponding RD spectra.

In contrast to relatively simple and easily aligned normal-incidence RD systems, the integrated RS/RC-PSCA ellipsometer, even though more powerful, is also more complicated and is sensitive to system artifacts that were not issues for simpler RAE and RPE ellipsometers. Since system errors are of the same order as anisotropy spectra, more care must be taken to eliminate noise and nonlinearity effects and therefore to obtain reasonable results. An example is the anomalous background that is linear in energy and needs to be subtracted from the data. Secondly, if the determinant of the matrix M is nearly singular, as is the case for long wavelengths, then sensitivity is reduced. This is the case for $P = 45^\circ$ $A = -45^\circ$, where the equivalent $\Delta r/r$ spectrum can be obtained but owing to the fact that the determinant of matrix M is nearly zero at 3.852 eV, the phase anisotropy $\Delta \theta$ has a singularity and cannot be determined.

Sample and mirror misalignments are other sources of error in anisotropy measurements. Sample wobble due to improper adjustment of its tilt angle is an effect peculiar to rotating-sample ellipsometers, and can have a large effect on the data as seen in Figure 5-18. Fortunately, the use of a secondary laser beam reflected off the sample allows this contribution to be reduced to small values. However, situations have arisen during deposition where the sample has warped at high temperatures, making such adjustments impossible.
Mirror adjustment is another factor. Optical systems are typically aligned using the criteria of maximum intensity, that is, mirrors are adjusted to give maximum intensity at the detector. However, in our RS/RC-PSCA ellipsometer we found that adjusting mirrors for maximum intensity can yield systematic errors that cannot be traced to system components such as the polarizer and analyzer. An extreme example of such errors is given in Figure 5-19, where 10ωt data for the cases of aligned and misaligned mirrors are compared. These effects can be minimized by adjusting the mirrors for minimal odd Fourier coefficients rather
than maximum intensity. In any case the difference in settings is not great. The effect appears to be due to the nonuniformity of the intensity across the beam.

Figure 5-19 Comparison of corrected $10\omega t$ spectra for $P = A = 0^\circ$ before and after the mirror in front of the spectrometer entrance slit was deliberately misaligned.

A particularly large result of a singularity in the inversion matrix for calculating equivalent normal-incidence spectra is shown in Figure 5-20. Here, the inversion for $\Delta\theta$ fails completely at 3.7 eV, as shown by the off-scale excursions and resultant clipping. This is a result of a combination of dielectric function values and system parameters. Gaps such as this can be bridged in principle by Kramers-Kronig transformations.
Figure 5-20. Determinant $M$ of $10\omega t$ coefficients is zero at 3.852 eV, and hence equivalent RD spectra has a singularity.

We conclude that normal- and non-normal-incidence data can be correlated, although some system errors are still being investigated.

5.3.1 Phase Relations Between the $a_{10}$ and $b_{10}$ Coefficients

The measured coefficients $\alpha_{10}$ and $\beta_{10}$ differ from the corresponding quantities used in theory by a phase factor that depends on pixel number, since there is a 5 $\mu$s time increment between readings. Using
\[ \phi = 2(\phi_0 + 5\omega t), \] (5.54)

we can write

\[ dc' = dc + a'_0 \cos(2(\phi_0 + 5\omega t)) + b'_0 \sin(2(\phi_0 + 5\omega t)), \] (5.55)

\[ dc' = dc + (a'_0 \cos(2\phi_0) + b'_0 \sin(2\phi_0)) \cos(10\omega t) + (b'_0 \cos(2\phi_0) - a'_0 \sin(2\phi_0)) \sin(10\omega t). \] (5.56)

Therefore

\[ a_{10,\text{data}} = a'_0 \cos(2\phi_0) + b'_0 \sin(2\phi_0), \] (5.57)

\[ b_{10,\text{data}} = b'_0 \cos(2\phi_0) - a'_0 \sin(2\phi_0). \] (5.58)

or alternatively

\[ a'_0 = a_{10,\text{data}} \cos(2\phi_0) - b_{10,\text{data}} \sin(2\phi_0), \] (5.59)

\[ b'_0 = a_{10,\text{data}} \sin(2\phi_0) + b_{10,\text{data}} \cos(2\phi_0). \] (5.60)

We find the phase reference \( \phi_o \) by taking data in the calibration configuration \( P = A = 0^\circ \) using the fact that under these conditions, \( b_{10} = 0 \) even although \( a_{10} \) can be nonzero depending on the anisotropy. Therefore \( \phi_o \) can be determined from

\[ 0 = a_{10,\text{data}} \sin(2\phi_0) + b_{10,\text{data}} \cos(2\phi_0), \] (5.61)

\[ \phi_0 = \frac{1}{2} \tan^{-1}\left( \frac{-b_{10,\text{data}}}{a_{10,\text{data}}} \right). \] (5.62)

The correction for the 5 \( \mu s \) interval between successive readings in the PDA corresponds to a phase lag of about 0.05\(^\circ\) in \( \phi_o \) between each pixel. This can either be assumed on the
grounds that the timer of the PDA controller is accurate, or be deduced from a linear fit to $\phi_o$ over the 1024 pixels.

Since the $\alpha_{10}$ and $\beta_{10}$ are normalized, it is expected that any background would be eliminated. However any system nonlinearity would result in a background (as is observed) and affect the data. This background must be subtracted from the phase corrected data. We do this as follows.

For $P = A = 0^\circ$, any nonzero contribution to $\beta_{10}$ is background and therefore needs to be subtracted from the $\beta_{10}$ data of the $P,A \neq 0$ configurations. This is an important issue because backgrounds here are observed to be of the same order as that of the anisotropy so the anisotropy spectra are directly affected by it. A similar background is present in the even Fourier coefficients. However since $2\omega_t$ and $4\omega_t$ are on the order of $10^3$ larger than the background, the resulting dielectric functions are not significantly affected.

Another factor is the choice of favorable values of $P$ and $A$ such that the conversion from the $10\omega_t$ to RDS spectra is possible. Although ideally any combination except $0^\circ$ and $90^\circ$ should work, not all the $P$ and $A$ values give acceptable results, possibly because of system misalignments and leakage.

5.4 Real-time Characterization of GaSb Epitaxy

In this section I illustrate an application of the instrumentation discussed above to the homo- and heteroepitaxial growth of moderately thick (~700 nm) layers of GaSb on (001)GaSb and (001)GaAs. This is a joint project involving several graduate students, and although I can operate the OMCVD reactor, my primary responsibility involved the acquisition and analysis of the optical data. Antimonides are potentially highly useful for low power device applications [24,25,26] However, the volatility of Sb is low, comparable to that of Al, Ga and In. [27] Thus excess Sb cannot be removed from the surface simply by heating, as is the case with the other Group-V elements. Excess Sb on to the surface causes roughness, whereas
excess Ga results in antisite defects and highly p-type material. [25,28] Thus without some kind of (optical) monitoring, it is impossible to establish proper growth conditions except by trial and error.

Therefore, GaSb growth represents an ideal application of real-time diagnostics. This work represents the first use of real-time SE to regulate antimonide growth. Although some real-time reflectance[29] and real-time RDS [30,31] data are available, the reflectance data are used mainly for thickness determinations and the RDS data are dominated by physical roughness (island) effects and cannot be used for analysis of the chemistry and kinetics of growth. The work discussed here has been presented [32] and published [33] elsewhere.

5.4.1 Homoepitaxy of GaSb Growth

For this work H₂ was used as a carrier gas with no filtering. Precursors were TMG and TMSb. The chamber pressure during growth was 60 torr. For the homoepitaxy work an epit-ready (001)GaSb substrate was cleaned by heating slowly to 700 °C to remove contamination and oxide overlayers. Growth was done with the sample at a temperature of 550 °C.

First, the stability of the (001)GaSb surface with respect to TMG and TMSb was considered. Because the growth is homoepitaxial, there is no optical contrast between substrate and overlayer, so the SE data are not affected by interference effects. Figure 5-21 shows ⟨ε₁⟩ and ⟨ε₂⟩ data at 1.91 and 3.56 eV respectively as a function of time for GaSb exposures at 550 °C to various precursor flow rates. The energy 3.56 eV was chosen because the E₂ peak occurs near this energy. The corresponding large absorption coefficient makes this wavelength useful for detecting the presence of overlayers and microscopic roughness. The initial roughness, as evidenced by the low value of both ⟨ε⟩ components, was due to overnight oxidation in the reactor, resulting in a rough surface as the oxide desorbed. At 690, 760, and 830 s into the run, TMG is introduced. Further surface roughening is observed as evidenced by decreases of both traces, indicating that the surface efficiently catalyzes the decomposition of the TMG precursor leaving metallic Ga. When TMG and TMSb are introduced simultaneously into the growth
chamber, growth occurs and the surface recovers. When TMG flow is terminated at 1260 s nothing happens, showing that the surface does not catalyze the decomposition of TMSb unless Ga is present and hence is stable in TMSb. The absence of both TMG and TMSb from 1269 to 1430 s again results in no degradation, which is expected because neither Ga nor Sb is volatile and hence neither would be expected to desorb. The instability to TMG was rechecked by turning TMG flow on for 3 s at 1430 s. The immediate reduction in value confirms that exposure of the surface to TMG in the absence of TMSb yields metallic Ga for smooth surfaces as well as rough surfaces.

Figure 5-21 Evolution of $\langle \varepsilon_1 \rangle$ and $\langle \varepsilon_2 \rangle$ at 1.91 and 3.56 eV, respectively, during homoepitaxy for an initially rough
(001)GaSb substrate with various exposures to TMG and TMSb indicated by G and S, respectively. G+S denotes growth, and H the halt to growth.

Since the decomposition thermodynamics of TMG and TMSb are similar and both are expected to decompose at 550 °C, these results show that TMSb does not chemisorb on the (001)GaSb surface.

A separate homepitaxial growth run was done to provide further details on optimum flow ratios of TMG and TMSb, therefore allowing us to optimize growth conditions. The data included light-scattering results to investigate the possible use of laser light scattering (LLS) to probe macroscopic surface roughness such as island or droplet formation. The complete growth record is shown as three-dimensional plots of $\langle e_1 \rangle$ and $\langle e_2 \rangle$ in Figure 5-22 and Figure 5-23. Our interest is mainly in the $E_2$ peak, which occurs near 300 nm. Figure 5-24 shows how the scattered light changes with several flow ratios, where minimum scattered intensity correlates with minimum macroscopic roughness. Flow ratios of 1.6, 4.1, 6.3, and 4.1 were instituted at 29, 36, 46, and 54 min. respectively. The flow ratio of 4.1 is observed to yield minimum macroscopic roughness, and in particular to improve surfaces that were roughened by growth under non-optimal conditions. This LLS result can be correlated with the $\langle e_2 \rangle$ plot of Figure 5-23, where the highest values correspond to the smoothest surfaces on a microscopic scale. The small difference in timing shows that microscopic roughness occurs first, followed by macroscopic roughness, as might be expected. For recovery, the microscopic signal recovers more quickly, which is again not surprising. The roughness data of the grown sample are in good agreement with with postgrowth AFM measurements [34].
Figure 5-22 3D plot of $\langle \varepsilon_1 \rangle$ during homoepitaxial growth of GaSb on(001)GaSb for various V/III flow ratios.
Figure 5-23 As Figure 5-223 but for $\langle \varepsilon_z \rangle$. 
Figure 5-24 LLS signal vs. time for various TMSb/TMG flow ratios is shown. The corresponding $\langle \varepsilon_2 \rangle$ 3D plot is shown in Figure 5-23.

5.4.2 Heteroepitaxy of GaSb on (001)GaAs

The heteroepitaxial growth of GaSb on (001)GaAs was also investigated. Experimental procedures were similar to those for homoepitaxial growth. Figure 5-25 and Figure 5-26 show the record of the real and imaginary parts of the pseudodielectric function in three dimensions with x- and y- axes being the time and wavelength of reflected light. We began the experiment by growing a buffer layer of GaAs with flow rates of 100 sccm ($4.5 \times 10^{-3}$ mol/s) of AsH$_3$ and 0.3 sccm ($1.35 \times 10^{-3}$ mol/s) of TMGa. This yielded a growth rate of 5.1
A°/s. The final thickness was 630 nm. The intention was to grow a compositionally graded interface layer by gradually adding TMSb to the flow then reducing the AsH₃ flow rate. TMSb was introduced at 7:35 min. at a flow rate of 0.50 sccm. No change was observed in the dielectric function as the flow rate of TMSb was increased from 0.50 sccm to 1.24 sccm in steps of 0.25 sccm in 7 min., indicating no Sb was being incorporated into the growing layer. We then decreased the AsH₃ flow, terminating it completely at 23:10. It is at this time that heteroepitaxial growth began, as can be seen in Figure 5-27, which provides a more detailed perspective by showing the trajectory of $\langle \varepsilon_2 \rangle$ vs. $\langle \varepsilon_1 \rangle$ with time as a running parameter. This is surprising, because it would be expected that Sb could compete successfully with As for the anion sites. However, the energy of the As-Ga bond, 210.0 kJ/mol, is larger than that of Sb-Ga bond, 191.6 kJ/mol, which may explain the lack of incorporation. Since only a finite amount of Sb would accumulate before being detected optically, the results actually suggest that TMSb was prevented from decomposing and simply desorbed.

As shown in Figs. 5-29, 5-30, and 5-31, the values of both real and imaginary parts of the pseudodielectric function drop rapidly during the initial stages of heteroepitaxy, then recover to values appropriate to GaSb. The reason for this is that growth does not proceed uniformly, but in the form of islands that initially form and are then filled in. The lowest values of $\langle \varepsilon \rangle$ correspond to the greatest fraction of voids within the layer, i.e., the least packing of islands, which occurs approximately 2 min into the run. This is supported by the anisotropy data of Fig. 5-32, which by the large value of $\alpha_{10}$ at this point shows that the resulting islands are in fact elongated in one direction. After reaching a minimum density the layer fills in and laminar growth returns. The change in the trajectory of Fig. 5-31 is due the return of the sample from growth to room temperatures. The data shown in Fig. 5-32 are actually a mixture of $\alpha_{10}$ and $\beta_{10}$, yet are useful for qualitative purposes because they show the evolution of the island microstructure from a different perspective.

An expanded view of the critical initial stage of heteroepitaxy is provided in Figure 5-28. This figure shows the thickness profiles as well as the evolution of growth from 23:14 to 24:04 min assuming that the overlayer consists of a Bruggeman effective-medium mixture of
GaAs, GaSb, and voids. Thickness profile shows an effective overall growth rate of about 5.15 A\(^0/s\), which is very close to the 3.9 A\(^0/s\) rate calculated from postgrowth analysis by SEM [33]. To obtain these results the material was described by the Bruggeman expression for a spherical inclusion geometry with values determined by least-squares analysis of the data. The calculated spectra are quite sensitive to the detailed values of the parameters, hence the parameters are determined fairly accurately.

The results provide a demonstration of the type of information obtainable from real-time measurements of the ellipsometric and anisotropic responses. Although not shown, TEM micrographs of the GaSb/GaAs interface showed no dislocations other than those necessary to accommodate the lattice mismatch between the two materials. AFM and electrical measurements verified that what was produced was high quality material. Thus the real-time measurements are useful in optimizing conditions for homo- and heteroepitaxial growth.
Figure 5-25 3D plot of $\langle \varepsilon_r \rangle$ during the heteroepitaxial growth of GaSb on (001)GaAs.
Figure 5-26 3D plot of $\langle \varepsilon_2 \rangle$ during heteroepitaxial growth of GaSb on (001)GaAs.
Figure 5-27 Growth record of GaSb on GaAs, presented as $\langle \varepsilon_r \rangle$ vs. $\langle \varepsilon_i \rangle$ at 1.96 eV, with time as a running parameter.
Figure 5-28 Evolution of void, GaAs, and GaSb fractions just following the onset of heteroepitaxial growth
Figure 5-29 The anisotropy record $\alpha_{10}$ during GaSb heteroepitaxy on (001)GaAs.
Chapter 6

6 CONCLUSIONS

Being nondestructive, optical diagnostics are being used increasingly in semiconductor technology for a wide range of applications. Because these applications require improvements in both diagnostic power and accuracy that are well beyond the capabilities of the RAE and RCE configurations that dominated the metrology field for the last 30 years, RAE and RPE ellipsometers are rapidly being replaced by rotating-compensator designs. As the RCE becomes more of an industry standard, it is important to determine exactly what are the limits of its accuracy, especially since an order-of-magnitude improvement in accuracy to the 0.1-0.2% range makes different classes of artifacts important. Further, the MgF$_2$ monoplate compensator, a recently invented component with particular advantages for the RCE, has not been analyzed previously. Finally, for real-time growth applications involving rotating samples, surface chemistry can be accessed through the optical anisotropy of the growth surface, which can be determined simultaneously on the integrated system that we have developed.

These topics all involve optical anisotropy in one form or another, whether related to optical components such as polarizers, compensators, or analyzers, or in the samples being measured. While crystal-optics is a topic that is well developed in the abstract sense, in this work we have found that the situation regarding practical applications is on a less secure
footing, so in addition to the specific results summarized below I have developed a mathematical procedure for eliminating singularities in the calculation of normal modes.

Specifically, I first consider the mathematical description of the problem. One of the most referenced works concerning the treatment of optically anisotropic materials in spectroscopic ellipsometry is the paper by Yeh, which follows Berreman's formulation in terms of operations by 4x4 matrices on mode vectors of $E$, and $H$ and gives a recipe for obtaining a general solution. However, the solution was unexpectedly found to be ill-conditioned in that for rotating samples, or for that matter optical elements with arbitrary crystal orientations and rotation azimuths in general, mode vectors calculated by Yeh’s approach vanish at certain azimuths, resulting in a singularity in the 4x4 solution of the system matrix for that optical element. I show how this limitation can be overcome and provide a detailed, mathematically robust analysis of the matrix method for wave propagation in laminar samples containing anisotropic materials. This solution can be applied to numerical analyses without the danger of encountering singularities, so the analysis of data obtained on optically anisotropic samples can now be considered routine.

In epitaxial growth the connection between growth chemistry and optical properties is made through the anisotropy of the growth surface, i.e., on a sub-nanometer scale. The effect of a thin anisotropic surface layer on an isotropic substrate was first considered by Hingerl et al. I present another solution based on a Taylor-series expansion of Maxwell’s Equations that avoids the need to solve the dispersion equation for the anisotropic layer. Since the results are identical to those obtained by Hingerl et al., the calculation is mainly of academic interest. However, these equations are investigated in detail for application to the integrated single-beam SE/anisotropy spectrometer that we developed for real-time diagnostics work in our OMCVD reactor. In contrast to literature speculations that non-normal-incidence measurements must contain bulk information, I find that the relevant Fourier sine coefficient carries no bulk information at all. This eliminates some apparent disadvantages of non-normal-incidence anisotropy measurements and enhances its attractiveness for real-time
Regarding system artifacts, I show that the treatment of axial misalignment requires an extension of the standard 2x2 Jones-matrix formulation to three dimensions. The 3x3-matrix treatment yields the corrections necessary for axially misaligned polarizers and analyzers, and forms the basis for a first-order analytic treatment of the properties of the misaligned monoplate compensator. The first-order calculations this gives great insight into monoplate data and how to correct data in general for system artifacts. The monoplate is a particularly interesting optical device because the odd harmonics of the Fourier expansion of the transmitted intensity provide information about the average propagation direction of the beam through the wave plate, and its dispersion equation is a quartic rather than the usual quadratic of a quadratic because the boundary conditions are coupled in. The calculation also resolves some puzzling features about monoplate measurements, for example the appearance of $1\omega_t$ and $3\omega_t$ sidebands in the intensity for slight misalignments under crossed-polarizer operation with no apparent $2\omega_t$ carrier frequency. The same technique can be applied to other configurations that may have system artifacts different from those investigated here. However, that is beyond the scope of the present project.

In summary, the work presented here gives considerable insight into the treatment of the properties of optically anisotropic materials in both data analysis and metrology instrumentation. It is expected to obtain immediate application for example for RT/CD work, and provides insights for the data analyses required for next-generation high-precision optical instrumentation.
NONLINEAR LEAST SQUARES METHOD

A description of nonlinear least square method is given, since this method is used widely in ellipsometric data analysis to determine the best fit of the experimental data to a model calculation.

The method can be described as follows: A model calculation is determined with number of parameters which is assumed to describe the experimental data. Then the difference between the acquired data and model calculation is minimized using the given parameters.

First step is to define a model, \( f(a,b,c,...;x_i) \), where \( f \) is the mathematical fitting function of the model, \( a,b,c,... \) are fitting parameters, \( x_i \) is the independent variable in the experiment. For simplicity we only consider two fitting parameters. Then error function can be written as,

\[
\delta^2 = \sum_{i}^N \left( f_i - f(a,b;x_i) \right)^2
\]

where \( N \) is the number of data points, \( f_i \). Minimizing \( \delta^2 \) with respect to fitting parameters \( a \) and \( b \),

\[
\frac{\partial \delta^2}{\partial a} = 0, \quad \frac{\partial \delta^2}{\partial b} = 0
\]

Next is to linearize the function \( f(a,b;x_i) \) around estimated values of \( a \) and \( b \) using \( a = a_0 + \Delta a \), \( b = b_0 + \Delta b \), where \( a_0 \) and \( b_0 \) are the estimated values of the parameters \( a \) and \( b \). Then using Taylor series expansion error function becomes
\[ \delta^2 = \sum_i^N \left\{ f_i - f(a_0, b_0; x_i) - \Delta a \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} - \Delta b \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right\}^2 \]

Then minimizing above equation with respect to \( \Delta a \) and \( \Delta b \)

\[ \frac{\partial \delta^2}{\partial \Delta a} = 0 = 2 \sum_i^N \left\{ f_i - f(a_0, b_0; x_i) - \Delta a \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} - \Delta b \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right\} \left( - \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} \right) \]

\[ \frac{\partial \delta^2}{\partial \Delta b} = 0 = 2 \sum_i^N \left\{ f_i - f(a_0, b_0; x_i) - \Delta a \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} - \Delta b \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right\} \left( - \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right) \]

Rearranging the terms, these equations can be written as the right side containing the parameters and lefts side with the experimental data and estimated function values

\[ \sum_i^N \left\{ f_i - f(a_0, b_0; x_i) \right\} \left( \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} \right) = \Delta a \sum_i^N \left( \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} \right)^2 + \Delta b \sum_i^N \left( \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right) \left( \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} \right) \]

\[ \sum_i^N \left\{ f_i - f(a_0, b_0; x_i) \right\} \left( \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right) = \Delta a \sum_i^N \left( \frac{\partial f}{\partial a} \bigg|_{a_0, b_0} \right) \left( \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right) + \Delta b \sum_i^N \left( \frac{\partial f}{\partial b} \bigg|_{a_0, b_0} \right)^2 \]

Above equation can be written in matrix form as

\[ \mathbf{Y} = \mathbf{M} \Delta \mathbf{X} \]

where \( \Delta \mathbf{X} \) is the vector containing parameters of the function \( f \). A simple matrix inversion results \( \Delta a \) and \( \Delta b \).

\[ \Delta \mathbf{X} = \mathbf{M}^{-1} \mathbf{Y} \]

A number of iterations can be used to improve the values of parameters by checking the error function as it should get smaller by improved results.

2. See for example J. D. Jackson, Classical Electrodynamics, 3rd Ed.

3. See for example Born and Wolf, Principals of Optics, 5th Ed.


18. See for example G. B. Arfken, Mathematical Methods for Physicists or H. Goldstein, Classical Mechanics

19. See for example G. B. Arfken, Mathematical Methods for Physicists


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