ABSTRACT

KLAUS FLOCK. Rotating Compensator Ellipsometry applied to OMCVD growth. (Under the direction of Prof. D. E. Aspnes.)

The objective of this research was to develop a better understanding of epitaxial growth through non-destructive real-time optical measurements. This required us to develop a rotating-compensator ellipsometer/polarimeter (RCE/RCP) integrated into a modified commercial organometallic chemical vapor deposition (OMCVD) system.

The new instrument obtains spectra of 1024 wavelengths (pixels) from 230 to 840 nm at a rate of 5 per second. The observables are the intensity of p- and s-polarized light, respectively, and the sine and cosine of the relative phase $\Delta$. The newer RCE technology removes a serious limitation of the previously employed rotating-polarizer (RPE) system, where the data is lost in the vicinity of $\Delta = 0$ and 180°.

By synchronizing the rotation of the substrate to the rotation of the compensator, we simultaneously measure the signal induced due to optical anisotropy of the sample. The connection between our non-normal-incidence anisotropy spectroscopy and normal-incidence reflectance difference spectroscopy (RDS) is established. As an example, the additional information is used to analyze a thin layer of Ga on a GaAs(001) substrate.

One of the major problems of optical real-time diagnostics is the simultaneous determination of the parameters $n$, $k$, and $d$, i.e., the complex refractive index and the thickness, respectively, of the most recently deposited material. I solve the problem by fitting an analytical representation to the lineshape of $n$ and $k$ as a function of $d$ in a region of the spectrum where $n$ and $k$ vary slowly with wavelength, i.e., in the region where the overlayer is transparent. The actual layer thickness is determined by the minimum of the merit function chi-square of the fit.

With the above approach to lineshape analysis, overlayer information is extracted post-acquisition from real-time data to characterize (1) a 0.11 nm layer of GaAs on
an AlGaAs substrate, and (2) a sequence of spectra recorded during the transition from AlGaAs to AlAs, where the deposition rate varied from $0.25 \text{ nm/s}$ to $1.35 \text{ nm/s}$ with increasing aluminum flux.
ROTATING COMPENSATOR ELLIPSOMETRY
APPLIED TO OMCVD GROWTH

by

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APPROVED BY:

[Signature]
Chair of Advisory Committee
To my family.
Biography

The author was born on August 10, 1972 in Roth, Germany, as the youngest of six children of Wolfgang and Kreszentia. He completed his secondary education at the Werner-von-Siemens-Gymnasium in Weissenburg (Germany) in 1992. After working carpenter and roofing jobs for a year he matriculated at the Technical University of Aachen and earned the pre-diploma in Physics in 1995. Following a one year stay at the University of Würzburg (Germany), he participated in an exchange program with the State University of New York at Buffalo, where he earned his Master’s Degree in Physics (1997). In spring of 1998 he enrolled in the Ph.D. program of the Department of Physics at North Carolina State University.
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Introduction

Metal Organic Chemical Vapor Deposition (MOCVD) was introduced by Manasevit [1] some twenty years ago and since then has evolved into a viable competitive technology that enjoys wide industrial acceptance. Applications that involve MOCVD systems range from simple processes to cutting-edge technology. Examples include the manufacture of diodes and transistors as well as light-emitting diodes, semiconductor lasers, and dielectric mirrors, respectively.

In a nutshell, during an OMCVD growth process small amounts of precursor molecules are transported in large volumes of carrier gas to the vicinity of a growth interface. Upon arrival at this interface, the precursors are cracked by means of pyrolytic decomposition and release the elemental species from which the growing semiconductor is assembled.

Precursors for group III (metallic-) elements, which are used frequently in OMCVD processes, are trimethylgallium (TMGa), trimethylaluminum (TMAI), and trimethylindium (TMIn). These examples of precursor species are formed from three methyl groups, which bond to a central metal atom. Instead of methyl groups, other organic compounds can be used, such as ethyl-, butyl-, propyl-, or dimethylamino- groups.

For group V sources, it is customary to use the hydride gases of the elements, in particular Phosphine ($PH_3$) and Arsine ($AsH_3$). Due to the toxicity of these
hydrides, however, there is also an ongoing effort to improve organic compound group V precursors to complement the group III materials. On the market available are trimethylarsine (TMAs), triethylphosphine (TEP), and trimethylantimony (TMSb), as well as compounds involving longer and more complex carbon groups.

A difficult challenge is the development of in-situ diagnostics to obtain information about the growing material in real time. Due to relatively high background pressures inside the OMCVD reactor during growth, which range from a few Torr to atmospheric pressures and beyond, the standard UHV diagnostic tools can not be applied. This contrasts the situation in MBE systems, where it is customary to use Rutherford High Energy Electron Diffraction (RHEED) and Low Energy Electron Diffraction (LEED) for in-situ diagnostics. The high scattering probability of electrons combined with the dense gaseous environment renders these tools useless for OMCVD growth.

In contrast, photons from the infrared to the near-UV exhibit a very weak interaction with the growth environment and are well suited for penetrating the reactor atmosphere during OMCVD growth. However, interpretation of the obtained optical data is difficult due to the fact that the information returned corresponds to the integrated response of the sample material over the penetration depth of light, which is of the order of the wavelength in absorbing regions and virtually infinite in regions where the sample is transparent. Accordingly, photons are not sensitive to the surface but return integrated bulk information with small contributions from the surface.

For diagnostics of thin-film deposition processes the large penetration depth of light leads to substantial complications since the near surface contributions, which are of particular interest, need to be isolated from the convoluted bulk and surface
signal by inverting systems of complicated, transcendental equations.

A particular problem that has not been solved yet is the simultaneous determination of the thickness and the complex index of refraction or, equivalently, the dielectric function of a depositing overlayer under real-time conditions. To address this problem, a specialized lineshape-analysis procedure has been developed, which is capable of extracting the desired overlayer parameters for sub-monolayer thicknesses. This approach makes deliberate use of the spectral capabilities of our system.

Surface information is also extracted indirectly by reflectance difference spectroscopy (RDS). The idea is to eliminate isotropic bulk contributions by taking the difference between reflected light that is polarized along the two principal axes of the surface, respectively. The isotropic contribution cancels out and the remaining signal is due to the optically induced anisotropy of the surface.

Our choice of optical diagnostics is ellipsometry. This is an old technique but it is currently undergoing a renaissance, which is driven in part by new detector technologies, in particular photo-diode-array- (PDA) and charge-coupled-device (CCD) detectors. In contrast to the older photomultiplier technology, PDA- and CCD-based systems can measure absolute intensities, which automatically combines ellipsometry and $p$- and $s$- polarized reflectometry into a single measurement, also known as polarimetry. These detectors also allow data to be acquired at all accessible wavelengths simultaneously, which enables parallel processing of all wavelengths, and which is essential for many real-time applications. Finally, the technology is moving toward the much more powerful but also much more challenging rotating compensator (RCE) configuration. As the original technology, null ellipsometry, was replaced some 15-20 years ago by rotating-polarizer (RPE) and rotating-analyzer (RAE) technologies
[2, 3], RPE and RAE systems are currently being replaced by RCEs.

When RCE systems are combined with a PDA or CCD detector, the four Stokes coefficients are detected simultaneously on a wavelength-by-wavelength basis, which means that the full information content of the accessible electromagnetic spectrum is extracted. In contrast to RPE and RAE systems, which are only sensitive to three of the four Stokes parameters, RCE systems measure the sign and the cosine of the relative phase $\Delta$ and, thereby, uniquely determine $\Delta$, which removes the previously encountered loss in data where $\Delta \approx 0$ or $180^\circ$. The only piece of information that is not accessible with present designs is the change in absolute phase of the electromagnetic field. This could only be determined by an interferometric measurement, which would require stabilities far beyond current or even foreseeable technologies.

The objectives of this project are (1) to investigate the capabilities and limitations of the RCE technology from a fundamental-physics perspective; (2) to implement a parallel-processing RCE as a data-acquisition and analysis module on an integrated OMCVD system, including hardware conception and design, in-house machining of all critical system components, hardware optimization, development of control software for the RCE, development of data-acquisition and data-analysis routines for continuous operation with simultaneous data-storage in real-time, and exploration of data analysis methods; (3) investigate whether the RCE has enough analytic power and accuracy to solve the remaining problem of determining thickness and dielectric function of the most recently deposited material under real-time growth conditions; (4) obtain a better connection between the optical-anisotropy signals measured at our current angle of incidence of $70^\circ$ and analogous data measured at normal incidence;
and (5) apply the capabilities to actual growth situations. We fully achieve goals (1), (2), (4), and (5), and show that goal (3) can be achieved by quantification of the well known method of residual lineshape analysis. I further show that the solution cannot be obtained with sufficient confidence on a wavelength-by-wavelength basis from so-called three parameter ellipsometry. Our results for goal (3) also reveal why electrochemists, who have attempted similar goals in more favorable modulation-spectroscopic configurations with stationary samples, were only partially successful. In essence, the understanding + technology that I have achieved here is clearly state-of-the-art.
Chapter 1

Mathematical foundation

1.1 Introduction

This chapter reviews necessary fundamentals of linear optics to establish the mathematical basis for this project in a compact form.

Section 1.2 states Maxwell’s equations together with a summary of the linear description of the interaction of light with matter. Section 1.3 is a discussion of the dispersion equation, which is a consequence of Maxwell’s equations, and its solution. The procedure for arriving at the optical response of a system/medium is presented here. The three-phase model is discussed in Sec. 1.4. In the last section 1.5 the complex reflectance ratio is defined and the optical quantities that we measure are identified.

1.2 Maxwell’s equations, linear optics, and dielectric response theory.

Classical electromagnetic theory is based on Maxwell’s equations. In their microscopic form, and for sources in vacuum, they are [4]
\[ \nabla \cdot \vec{E} = 4\pi \rho, \]
\[ \nabla \times \vec{B} - \frac{1}{c} \frac{\partial \vec{E}}{\partial t} = \frac{4\pi}{c} \vec{j}, \]
\[ \nabla \times \vec{E} + \frac{1}{c} \frac{\partial \vec{B}}{\partial t} = 0, \]
\[ \nabla \cdot \vec{B} = 0, \]

where \( c \) is the speed of light,\(^1 \vec{j} = \rho \vec{v} \) is the current density, and \( \rho \) is the charge density.

**Macroscopic Fields**

Macroscopic fields are those resulting from suitable averages over the microscopic fields associated with a collection of charges. Averages are typically done over both space and time. While “macroscopic” is not a well-defined term, spatial averages are commonly done over volumes that contain a “large” number of sources (atoms) but that are still small compared to the wavelength of the (propagating) fields and more specifically small compared to the inhomogeneities of the material (-system) in which we are interested. The goal is to retain adequate resolution to spatial variations while avoiding uninteresting detail.

**Linearity and Susceptibilities**

Since Maxwell’s equations are linear, fields are automatically additive. However, “linear” in “linear optics” does not refer to the linearity of Maxwell’s equations but to the linear response of matter to an applied electromagnetic field. From the classical perspective, matter consists of a collection of charges, dipoles, and higher moments,
that can be driven by internal or external fields. Driving these charges creates dipoles, which in the linear approximation radiate at the drive frequency. These fields also interact with the charges, thus making the problem although linear, also self-consistent. Not surprisingly, linear optics corresponds to field strengths small enough so that the charges inside the medium undergo merely harmonic displacements. The intensities we use all fall into this category.

Accordingly, the task of determining interactions of light with matter becomes one of finding a microscopic self-consistent solution to a given ‘steady-state’ situation of internal and external fields and ultimately expressing the result in macroscopic form. In the averaging process we single out the polarization and magnetization that are induced by the external field and represent them by the dielectric and magnetic susceptibilities $\chi_e$ and $\chi_m$, respectively. When incorporated into the averaged (macroscopic) form of Maxwell’s equations, it is useful to combine these with the driving fields and define two new quantities, the dielectric function $\epsilon$ and the magnetic permeability $\mu$ according to

$$\vec{D} = \vec{E} + 4\pi\vec{P} = \vec{E} + 4\pi\bar{\chi}_e\vec{E} = \tilde{\epsilon}\vec{E}$$
$$\vec{B} = \vec{H} + 4\pi\vec{M} = \vec{H} + 4\pi\bar{\chi}_m\vec{B} = \tilde{\mu}\vec{H},$$

where $\vec{D}$ and $\vec{H}$ are called the electric displacement field and the magnetic field, respectively. In practice a magnetic dipole cannot follow optical frequencies, so we can set $\mu = 1$ in the following. A medium is said to be isotropic if $\vec{P}$ is always parallel (anti-parallel) to the applied field, regardless of its orientation. In general, this is not the case on the microscopic scale since the bond response depends on the orientation of the applied field. However, if the macroscopic symmetry of the
material is sufficiently high, for example cubic, the microscopic effects average out and the overall response is isotropic. For lower-symmetry situations this is generally not the case and $\chi_\epsilon$ is a second-rank tensor, as indicated by the tilde symbol in Eq. (1.2.2).

From a classical perspective, electromagnetic probes return information about the $\chi_\epsilon$ or equivalently $\epsilon$, which from the above discussion clearly encodes information about the material.

1.3 The dispersion equation and reflectances

When combined, the two Maxwell equations that contain the curl operator yield the dispersion equation, which describes the propagation of light through a linear medium:

$$-\nabla \left( \nabla \cdot \vec{E} \right) + \nabla^2 \vec{E} + \tilde{\epsilon} \omega^2 \frac{\vec{E}}{c^2} = 0.$$  
(1.3.1)

We write $\tilde{\epsilon}$ as a tensor quantity, indicating that the propagation of light may depend on the direction of polarization. Since the magnitude of the electric field enters Eq. (1.3.1) only as a scaling parameter, we have a classical eigenvalue/eigenmode problem with the solutions being of the form $\vec{E}_0 e^{i\vec{k} \cdot \vec{r} - i\omega t}$, where $\vec{E}_0$ represents an eigenmode and $k$ the associated eigenvalue. A general electromagnetic wave is a linear combination (superposition) of these solutions.

Isotropic media are characterized by a diagonal $\epsilon$-tensor with all elements equal. In that case, the tensor reduces to a scalar and the eigenmodes become degenerate (have the same value of $k$) and are required only to be perpendicular to $\vec{k}$. The propagation speed of light in the material is given by $c/n$, where $n = \sqrt{\epsilon}$ is the
complex index of refraction.

Having the propagation modes, we now calculate the reflectances by matching incident, reflected, and transmitted waves at the a planar boundary using the standard boundary conditions. The solution is expressed in terms of the complex quantities $\tilde{r}$ and $\tilde{t}$, which are the reflection and transmission coefficients, respectively, for an applied electromagnetic field.

The case of a homogeneous medium is relatively easy to solve, especially if the medium is also isotropic. For convenience, I define the projection of the refractive index perpendicular to the surface as $n_{i,\perp} = \sqrt{\epsilon_i - \epsilon_a \sin^2 \theta}$, where $\epsilon_i$ is the dielectric function of any of the layers of the sample, $\epsilon_a$ is the dielectric function of the ambient, and $\theta$ is the angle of incidence. In particular,

$$n_{a,\perp} = \sqrt{\epsilon_a - \epsilon_a \sin^2 \theta} = n_a \cos \theta, \tag{1.3.2}$$

$$n_{s,\perp} = \sqrt{\epsilon_s - \epsilon_s \sin^2 \theta},$$

where $\epsilon_s$ is the dielectric function of the substrate.

The solutions for the complex field reflectances $\tilde{r}_p$ and $\tilde{r}_s$ for an isotropic, homogeneous medium adjacent to an ambient medium – the so-called two-phase (substrate-ambient) model – are

$$\tilde{r}_p = \frac{E_{out}^p}{E_{in}^p} = \frac{\epsilon_s n_{a,\perp} - \epsilon_a n_{s,\perp}}{\epsilon_s n_{a,\perp} + \epsilon_a n_{s,\perp}}, \tag{1.3.3}$$

$$\tilde{r}_s = \frac{E_{out}^s}{E_{in}^s} = \frac{n_{a,\perp} - n_{s,\perp}}{n_{a,\perp} + n_{s,\perp}}, \tag{1.3.4}$$

where the subscripts $p$ and $s$ refer to $p-$ and $s-$polarization, respectively.
1.4 The three-phase model

The next generalization is the three-phase (substrate-overlayer-ambient) model, which is used extensively throughout this research. It consists of a substrate defined as being optically opaque, an overlayer, and an isotropic ambient, e.g., vacuum, air, or, as in this research, the growth environment inside an OMCVD reactor. The complex reflection coefficients for this system are given by [5]

\[
\tilde{r}_{(p,s)} = \tilde{r}_{oa,(p,s)} + \tilde{r}_{so,(p,s)} Z,
\]

(1.4.1)

where \( Z = e^{2ik_{o,z}d} \), and \( \tilde{r}_{oa,(p,s)} \) and \( \tilde{r}_{so,(p,s)} \) are the complex reflection coefficients for the overlayer-ambient and substrate-overlayer interfaces, respectively, calculated in the two phase model:

\[
\tilde{r}_{oa,p} = \frac{\epsilon_o n_{a,\perp} - \epsilon_a n_{o,\perp}}{\epsilon_o n_{a,\perp} + \epsilon_a n_{o,\perp}}, \quad \tilde{r}_{oa,s} = \frac{n_{o,\perp} - n_{o,\perp}}{n_{o,\perp} + n_{o,\perp}}
\]

(1.4.2)

\[
\tilde{r}_{so,p} = \frac{\epsilon_s n_{o,\perp} - \epsilon_o n_{s,\perp}}{\epsilon_s n_{o,\perp} + \epsilon_o n_{s,\perp}}, \quad \tilde{r}_{oa,s} = \frac{n_{o,\perp} - n_{s,\perp}}{n_{o,\perp} + n_{s,\perp}}.
\]

More complicated samples can be described by using multiple layers of stratified material. In this case, each layer contributes its own set of reflection and transmission coefficients and phase terms \( Z = e^{ik_{i,z}d_i} \) for transmitted and back-reflected waves. Here, \( d_i \) is the layer thickness, \( k_{i,z} \) is the \( z \)-component of the wave vector within the layer \( i \), i.e., the projection of the wave vector onto the surface normal, which can be positive or negative, depending on the direction of propagation.

For reflection measurements the goal is to find the effective values for \( \tilde{r}_p \) and \( \tilde{r}_s \).
of the composite structure. It is not possible with present technology to measure \( \tilde{r}_p \) and \( \tilde{r}_s \) directly. Instead, one measures the power reflectance \( R = \frac{I^{in}/I^{out}}{|E^{out}|^2/|E^{in}|^2} = |r|^2 \), where \( r \) can be either \( r_p \), \( r_s \), or the normal-incidence limit.

In ellipsometry one deals with polarization states, defined as the ratios \( \chi = E_x/E_y \), where \( E_x \) and \( E_y \) are the projections of a field in a suitable coordinate system. Usually these are the \( p- \) and \( s- \) polarized components \( E_p \) and \( E_s \), such that \( \chi = E_p/E_s \). In ellipsometry one typically establishes a given polarization state, reflects the beam of light from the sample surface, and then analyzes the reflected beam for its new polarization state. Then the ratio

\[
\frac{\chi_{out}}{\chi_{in}} = \frac{E_{out}^{p}/E_{out}^{s}}{E_{in}^{p}/E_{in}^{s}} = \frac{\tilde{r}_p}{\tilde{r}_s} = \tilde{\rho} = \tan \psi e^{i\Delta}, \tag{1.4.3}
\]

is calculated, where \( \tan \psi \) is the amplitude and \( \Delta \) is the phase. This ratio is often expressed as the pseudo dielectric function \( <\epsilon> \), which is related to \( \tilde{\rho} \) by

\[
<\epsilon> = \left( \frac{\rho - 1}{\rho + 1} \right)^2 \tan^2 \theta \sin^2 \theta + \sin^2 \theta. \tag{1.4.4}
\]

1.5 Optical measurements

For optical diagnostics involving propagation of light through air, the following considerations are important. (1) Air is an isotropic medium, which implies that the electric field is always perpendicular to \( \vec{k} \), so that the field vectors can be represented in a two dimensional plane perpendicular to \( \vec{k} \). (2) It is possible in practice to measure three independent quantities: (1) the intensity of p-polarized light, (2) the intensity of s-polarized light, and (3) the complex field ratio \( \tilde{E}_p/\tilde{E}_s \), which yields the relative phase \( \Delta \) between p- and s-polarized waves. As mentioned above, a fourth parameter,
i.e., the absolute phase, cannot be measured under OMCVD conditions with present technology. The three measurable quantities can be combined into

In our RCE configuration we measure in principle all three of these quantities, so that the RCE is actually a polarimeter instead of an ellipsometer. This follows because the output of the photodiodes is linear in the number of photons that arrive during the integration time of the diode, i.e., the detector response is proportional to intensity. The connection between these measurables and the sample is the subject of Ch. 2.
Chapter 2

Rotating compensator ellipsometer (RCE) – system theory

2.1 Jones-matrix formalism

The transmitted signal of the RCE can be calculated in the Jones-matrix formalism, where each optical element is represented by a $2 \times 2$ matrix. The detected signal is obtained in the following way: (1) the so-called system matrix is derived by multiplying the representations for all optical elements in the order in which they are configured; (2) the transmitted electric field vector follows by multiplying the system matrix into the incident field vector; (3) the detected signal (intensity) is obtained from the absolute square of the electric field followed by averaging over the integration time of the detector, the cross-section of the beam, and the wavelengths reaching the detector. However, I neglect the latter two averages since in the present experiment they have no appreciable influence on the signal.

2.1.1 Ideal optical elements

For reflection at non-normal incidence, it is convenient to define an orthonormal reference frame with $\hat{x}$ and $\hat{y}$ parallel and perpendicular, respectively, to the plane of
incidence, and $\hat{z}$ along the direction of $\vec{k}$. An electric field vector is expressed as

$$\vec{E} = \begin{pmatrix} \tilde{E}_p \\ \tilde{E}_s \end{pmatrix},$$

(2.1.1)

where the subscripts $p$ and $s$ indicate polarizations parallel and perpendicular, respectively, to the plane of incidence.

The optical elements that enter the description of the RCE system in the form of Jones matrices are (1) the polarizer, (2) the sample, (3) the compensator, and (4) the analyzer. The reactor windows are here treated as being neutral, i.e., their transformation is considered to be that of the $2 \times 2$ unit matrix.

An ideal polarizer passes the electric field component that is parallel to its transmission axis and rejects the perpendicular component. An ideal analyzer does the same, and so the Jones matrices for polarizer and analyzer are given in the ideal case by

$$\tilde{P}, \tilde{A} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}.$$

(2.1.2)

The compensator introduces a relative phase shift $\delta$ between the two orthogonal directions of polarization, $E_p$ and $E_s$. The matrix representation of an ideal compensator can be written

$$\tilde{C} = \begin{pmatrix} e^{i\delta/2} & 0 \\ 0 & e^{-i\delta/2} \end{pmatrix}.$$

(2.1.3)

In the case of isotropic reflection, the sample is represented by the matrix

$$\tilde{S} = \begin{pmatrix} \tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{pmatrix}.$$

(2.1.4)
When the sample is anisotropic, \( r_p \) and \( r_s \) become functions of the orientation \( \phi_S \) of the crystal relative to the plane of incidence and the off-diagonal elements in general no longer vanish as a result of anisotropy-induced mixing of polarization states. We consider here only the most elementary form of anisotropy, that of a surface layer.

The representations for polarizer and analyzer (2.1.2) and for the compensator (2.1.3) correspond to the special case where the transmission or primary axis is aligned with the plane of incidence, respectively. During operation of the RCE this is not the case. The elements are actually oriented with their axes away from the plane of incidence, e.g., usually 45° and −45° for polarizer and analyzer, respectively, and with of the compensator rotating continuously. Therefore, the element matrices must be accompanied by rotation matrices \( \tilde{R} \) and \( \tilde{R}^{-1} \), which are denoted by \( \tilde{R}_P \) for the polarizer, \( \tilde{R}_C \) for the compensator, and \( \tilde{R}_A \) for the analyzer where for example

\[
R_A = \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix}.
\]  
(2.1.5)

The respective azimuths \( P, C, \) and \( A \) are referenced to the plane of incidence.

### 2.1.2 System matrix and transmitted intensity

The system matrix \( \tilde{J} \) is given by

\[
\tilde{J} = \tilde{A} \tilde{R}_A \tilde{R}_C^{-1} \tilde{C} \tilde{R}_C \tilde{S} \tilde{R}_P \tilde{P}.
\]  
(2.1.6)

The product can be evaluated explicitly by substituting the expressions for the optical elements and the rotation matrices from from the previous section into Eq. (2.1.6):
\[ \tilde{J} = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \begin{pmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{pmatrix} \begin{pmatrix} \cos C & -\sin C \\ \sin C & \cos C \end{pmatrix} \times \]
\[ \times \begin{pmatrix} e^{i\delta/2} & 0 \\ 0 & e^{-i\delta/2} \end{pmatrix} \begin{pmatrix} \cos C & \sin C \\ -\sin C & \cos C \end{pmatrix} \begin{pmatrix} \tilde{r}_p & 0 \\ 0 & \tilde{r}_s \end{pmatrix} \times \]
\[ \times \begin{pmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}. \]

(2.1.7)

With these ideal elements, the system matrix has the form

\[ \tilde{J} = \begin{pmatrix} J_{11} & 0 \\ 0 & 0 \end{pmatrix}, \]

(2.1.8)

with \(J_{11}\) given by

\[ J_{11} = \tilde{r}_p \cos P \left( \cos \frac{\delta}{2} \cos A + i \sin \frac{\delta}{2} \cos (2C - A) \right) \]
\[ + \tilde{r}_s \sin P \left( i \sin \frac{\delta}{2} \sin A + \cos \frac{\delta}{2} \sin (2C - A) \right). \]

(2.1.9)

The transmitted electric field follows by multiplying the system matrix into the incident field vector:

\[ \begin{pmatrix} \tilde{E}_p \\ \tilde{E}_s \end{pmatrix}_{\text{out}} = \tilde{J} \begin{pmatrix} \tilde{E}_p \\ \tilde{E}_s \end{pmatrix}_{\text{in}} = \begin{pmatrix} J_{11} E_{p,\text{in}} \\ 0 \end{pmatrix}. \]

(2.1.10)

The transmitted intensity follows by taking the absolute square of \(\tilde{E}_{out}\)

\[ I_{out} \propto |E_{out}|^2 = |J_{11} E_{p,\text{in}}|^2. \]

(2.1.11)

After substituting \(J_{11}\) from Eq. (2.1.9), the ratio of output to input intensity can be expressed in various ways:
\[ I_{\text{out}} / I_{\text{in}} = \]
\[ |r'_p|^2 f_1 (C) + |r'_s|^2 f_2 (C) + Re \left( \tilde{r}'_p \tilde{r}'_s^* \right) f_3 (C) + Im \left( \tilde{r}'_p \tilde{r}'_s^* \right) f_4 (C), \]  
(a)
\[
\alpha_0 + \alpha_2 \cos 2C + \beta_2 \sin 2C + \alpha_4 \cos 4C + \beta_4 \sin 4C, \]  
(b)
\[
c_0 + c_2 \cos (2C - 2A) + s_2 \sin (2C - 2A) + c_4 \cos (4C - 2A) + s_4 \sin (4C - 2A), \]  
(c)
\[
(2.1.12)\]

The above equation defines various functions and coefficients that will be used later:

(1) The functions \( f_1 (C), \ldots, f_4 (C) \) summarize in the most fundamental way how the intensity depends on the sample properties in the isotropic case;

(2) The coefficients \( \alpha_0, \ldots, \beta_4 \) describe the standard Fourier expansion of Eq. (2.1.11) referenced to the plane of incidence;

(3) As (2) but referenced to the azimuthal angle \( 2A \).

From Eq. (2.1.12 a) it is clear that the most fundamental sample properties that we can access with the RCE are \( |r'_p|^2, |r'_s|^2, \) and \( \tilde{r}'_p \tilde{r}'_s^* \). These quantities are not independent, since
\[
\left[ 2Re \left( \tilde{r}'_p \tilde{r}'_s^* \right) \right]^2 + \left[ 2Im \left( \tilde{r}'_p \tilde{r}'_s^* \right) \right]^2 = |r'_p|^2 |r'_s|^2. \]

We note that this leads immediately to a self-consistency relation that will later take the form of the Schwartz inequality for the Stokes parameters. A fourth quantity would be the absolute phase, but this is lost in an intensity measurement. Equation (2.1.11 c), an alternate form of Eq. (2.1.11 b), leads to simpler analytic representations when first-order corrections for the system artifacts are considered. The coefficients \( \alpha_0, \ldots, \beta_4 \) are given explicitly by
\[ \alpha_2 = - \sin(\delta) \, \text{Im} \left( \tilde{r}_p' \tilde{r}_s'^* \right) \sin 2A, \]
\[ \beta_2 = + \sin(\delta) \, \text{Im} \left( \tilde{r}_p' \tilde{r}_s'^* \right) \cos 2A, \]
\[ \alpha_4 = \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |\tilde{r}_p'|^2 - |\tilde{r}_s'|^2 \right) \cos 2A - 2 \text{Re} \left( \tilde{r}_p' \tilde{r}_s'^* \right) \sin 2A \right], \]
\[ \beta_4 = \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |\tilde{r}_p'|^2 - |\tilde{r}_s'|^2 \right) \cos 2A + 2 \text{Re} \left( \tilde{r}_p' \tilde{r}_s'^* \right) \sin 2A \right], \]
\[ \alpha_0 = \frac{1}{2} \left[ \left( |\tilde{r}_p'|^2 + |\tilde{r}_s'|^2 \right) + \cos^2 \left( \frac{\delta}{2} \right) \left[ \left( |\tilde{r}_p'|^2 - |\tilde{r}_s'|^2 \right) \cos 2A + 2 \text{Re} \left( \tilde{r}_p' \tilde{r}_s'^* \right) \sin 2A \right] \right], \]

(2.1.13)

### 2.1.3 Stokes parameters and Schwartz inequality

For unit magnitude \( |\widetilde{E}_\text{in}|^2 = 1 \) of the incident electric field, the Stokes parameters are related to \( r_p' \) and \( r_s' \) of the transmitted intensity by:

\[
\begin{align*}
    s_0 &\equiv |E_p|^2 + |E_s|^2 = |\tilde{r}_p'|^2 + |\tilde{r}_s'|^2 \\
    s_1 &\equiv |E_p|^2 - |E_s|^2 = |\tilde{r}_p'|^2 - |\tilde{r}_s'|^2 \\
    s_2 + is_3 &\equiv E_p E_s^* = \tilde{r}_p' \tilde{r}_s'^*. \quad (2.1.14)
\end{align*}
\]

The extra information from the cross term \( \tilde{r}_p' \tilde{r}_s'^* \) is the relative phase \( \Delta \) between the \( p- \) and \( s- \) polarized waves.

Equation (2.1.13) for the Fourier coefficients can be written in terms of the Stokes parameters as follows:
\[ \alpha_2 = \frac{i}{2} \sin (\delta) s_3 \sin 2A, \]
\[ \beta_2 = -\frac{i}{2} \sin (\delta) s_3 \cos 2A, \]
\[ \alpha_4 = \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) (s_1 \cos 2A - s_2 \sin 2A), \]
\[ \beta_4 = \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) (s_1 \sin 2A + s_2 \cos 2A), \]
\[ \alpha_0 = \frac{1}{2} \left[ s_0 + \cos^2 \left( \frac{\delta}{2} \right) (s_1 \cos 2A + s_2 \sin 2A) \right], \]

Inverting the equations yields the analytic expressions for the Stokes parameters as functions of the Fourier coefficients:

\[
\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} = \frac{2}{\sin^2 \left( \frac{\delta}{2} \right)} \begin{pmatrix} \cos 2A & \sin 2A \\ -\sin 2A & \cos 2A \end{pmatrix} \begin{pmatrix} \alpha_4 \\ \beta_4 \end{pmatrix},
\]
\[ is_3 = \frac{2}{\sin \delta} (\alpha_2 \sin 2A - \beta_2 \cos 2A), \]
\[ s_0 = 2\alpha_0 - \cos^2 \left( \frac{\delta}{2} \right) (s_1 \cos 2A + s_2 \sin 2A) \]

The Stokes parameters are not independent, since they are defined in terms of the three quantities, \(|r_p'|^2\), \(|r_s'|^2\), and \(r_p' r_s'^*\) (Eq. 2.1.14). The relationship between the parameters is expressed with the so-called Schwartz inequality as

\[ \eta \leq \frac{s_1^2 + s_2^2 + s_3^2}{s_0^2} \leq 1, \]

where \(\eta\) is called the degree of polarization. At any instant, the degree of polarization is always one, because a given field is always in a well-defined state of polarization. The concept of a degree of polarization makes sense only within the context of an optical detector that time averages the incoming signal over a specific interval. In
that sense, $\eta = 0$ corresponds to a sequence of photons with no field direction or phase coherence, a condition that is referred to as unpolarized light. $\eta = 1$ means that all photons are in the same state of polarization, e.g., after the photons have passed through an ideal polarizer. For a real application, which involves polarized light but also includes the possibility of depolarization due to non-ideal optical elements including the sample, the degree of polarization lies between 0 and 1.

The advantages of rotating-compensator ellipsometers over rotating-analyzer- and rotating-polarizer systems are (1) the sign of $\Delta$ is determined by the real and the imaginary parts of $\tilde{r}_p^f \tilde{r}_s^{f\ast}$, and (2) the Schwartz inequality is available both to self-analyze the system for depolarizing phenomena, e.g., polarizer leakage and scattering, and to obtain additional information about the measured sample.

The transmitted intensity of an RPE system is

$$\frac{I_{out}}{I_{in}} = \frac{1}{2} \left( s_0 + s_1 \cos 2P + s_2 \sin 2P \right). \quad (2.1.18)$$

Thus, for a RPE only three of the four Stokes parameters are available. The phase $\Delta$ is obtained as $\cos \Delta$ from $s_2 = 2 \text{Re} \left( \tilde{r}_p^f \tilde{r}_s^{f\ast} \right)$. However, the cosine is an even function so, as is well known, the sign of $\Delta$ cannot be determined an RPE. This is a particular problem in the transparent region of an overlayer, since measured interference oscillations appear rectified, which makes the data difficult to analyze. Further, RPE/RAE systems fail to return useful information if $\Delta \approx 0, 180^\circ$, since the cosine function is insensitive to small changes in $\Delta$ at these values. Finally, the degree of polarization cannot be determined from Eq. (2.1.18), and hence the Schwartz inequality is not available to investigate depolarization effects and for self-analysis of the instrument.
2.2 Actual elements

The treatment above outlines the ideal RCE system and the ideal result for the transmitted intensity. However, actual optical elements are not ideal but exhibit artifacts such as leakage, scattering, and in the case of crystalline quartz, optical activity. Since our polarizer and analyzer prisms are made from crystalline quartz, the effect of optical activity needs to be included here. For optically active material the propagation modes of the polarizer are slightly elliptical and project into the laboratory frame according to the relation

\[
\begin{pmatrix}
E_x \\
E_y
\end{pmatrix}
= \begin{pmatrix}
1 & i\gamma_p \\
i\gamma_p & 1
\end{pmatrix}
\begin{pmatrix}
E_u \\
E_v
\end{pmatrix},
\]  
\(2.2.1\)

The ideal polarizer transmits \(E_u\) and blocks \(E_v\), whence if the incoming field vector is \((E_a, E_b)\) the outgoing field vector \((E_u, E_v)\) is

\[
\begin{pmatrix}
E_u \\
E_v
\end{pmatrix}
= \begin{pmatrix}
1 & 0 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
E_a \\
E_b
\end{pmatrix}.
\]  
\(2.2.2\)

However, leakage has the effect that not all perpendicular components of the incident light are rejected, but small amounts are mixed into the nominally transmitted beam. In addition, scattering at the interface of the two prism halves can lead to crosstalk, i.e., an \(x\)– component may scatter into the \(y\)– component, and vice versa. Thus, the action of an imperfect polarizer fabricated from optically active material can be represented by the matrix product

\[
\tilde{P} = \begin{pmatrix}
1 & i\gamma_p \\
i\gamma_p & 1
\end{pmatrix}
\begin{pmatrix}
1 & l_{xy} \\
l_{yx} & 1
\end{pmatrix},
\]  
\(2.2.3\)

where the matrix on the left projects the elliptical eigenmodes of the prism into
the laboratory $x, y$-frame and the matrix on the right quantifies the possible leakage and scattering channels within the polarizer. $\gamma_p$ is the wavelength dependent value for the effect of optical activity ($\approx 10^{-3}/(eV)$), $l_{xy}$ and $l_{yx}$ are the probabilities for scattering from one polarization state into the other, respectively, and $l_{yy}$ is the leakage term, that mixes the nominally rejected component into the transmitted beam. After multiplication $\tilde{P}$ takes the explicit form

$$\tilde{P} = \begin{pmatrix} 1 + i\gamma_p l_{yx} & l_{xy} + i\gamma_p l_{yy} \\ i\gamma_p + l_{xy} & i\gamma_p l_{xy} + l_{yy} \end{pmatrix}. \tag{2.2.4}$$

I assume that the crosstalk terms $l_{xy}$ and $l_{yx}$ are negligible for present purposes. Further, I ignore second order corrections of the form $\gamma_p l_{xy}$. The leakage term $l_{yy}$ also enters the expression for the transmitted intensity as a second order term, so I also ignore it at this point. What remains is the contribution $\gamma_p$ from optical activity. The matrix for the actual polarizer now simplifies to

$$\tilde{P} = \begin{pmatrix} 1 & 0 \\ i\gamma_p & 0 \end{pmatrix}. \tag{2.2.5}$$

The above discussion carries over to the analyzer whose resulting matrix representation is given by

$$\tilde{A} = \begin{pmatrix} 1 & -i\gamma_a \\ 0 & 0 \end{pmatrix}. \tag{2.2.6}$$

Note, that the sign of $\gamma_a$ is different from that of $\gamma_p$, which is a consequence of the fact that the laboratory field components must now be projected into the elliptical modes of the analyzer.
2.2.1 Optical activity corrections

I now consider explicit expressions for the effect of optical activity on the detected intensity, first for the polarizer, then the analyzer.

**Polarizer**

Substituting the polarizer matrix (2.2.5) into Eq. (2.1.7), and combining it with the rotation matrix, the polarizer representation is given by

\[
\tilde{R}_P \tilde{P} = \begin{pmatrix}
\cos P - iγ_p \sin P & 0 \\
\sin P + iγ_p \cos P & 0
\end{pmatrix}.
\]  

(2.2.7)

Therefore, the correction to the transmitted intensity is contained in the values for \( r'_p \) and \( r'_s \), which now take the form

\[
r'_p = r_p (\cos P - iγ_p \sin P)
\]

\[
r'_s = r_s (\sin P + iγ_p \cos P).
\]

(2.2.8)

To first order in \( γ_p \), our observables are

\[
|r'_p|^2 = |r_p|^2 \cos^2 P,
\]

\[
|r'_s|^2 = |r_s|^2 \sin^2 P,
\]

(2.2.9)

\[
r'_p r'_s^* = \frac{1}{2} r_p r_s^* \sin 2P + iγ_p r_p r_s^*.
\]

Thus, to first order in \( γ_p \) the Stokes parameters \( s_0 \) and \( s_1 \) are not affected by the activity of the polarizer prism.

**Analyzer**

The optical activity corrections due to the analyzer are more difficult to derive since they are not connected to \( r'_p \) and \( r'_s \) in the simple way of the polarizer. Instead of
presenting the derivation, which is about 7 handwritten pages long, I simply state
the results for the correction $\delta I_{\gamma a}$ to the intensity ratio $I_{\text{out}}/I_{\text{in}}$:

$$\frac{\delta I_{\gamma a}}{I_{\text{in}}} = \gamma_a \left(2\text{Re} \left( \tilde{r}_p^l \tilde{r}_s^l \right) \right) \sin \delta$$

$$+ \gamma_a \left(2\text{Im} \left( \tilde{r}_p^l \tilde{r}_s^l \right) \right) \cos 2C \cos \delta$$

$$+ \gamma_a \left( |\tilde{r}_p^l|^2 + |\tilde{r}_s^l|^2 \right) \sin 2C \sin \delta. \tag{2.2.10}$$

Interestingly, there is no first order contribution to the $4\omega t$ coefficients $\alpha_4$ and $\beta_4$.

For the ideal system $\alpha_2$ and $\beta_2$ are symmetric. This conditions remains even when
optical activity of the polarizer is included to first order. However, the analyzer prism
breaks this symmetry. The two coefficients are independent to the extent of the first
order optical activity contribution of the analyzer.
Chapter 3

Anisotropy spectroscopy

For optically anisotropic materials the reflection properties become a function of the sample azimuth relative to the plane of incidence. Since our substrate is rotating continuously, a contribution due to optical anisotropy is encoded in the spectrum of Fourier coefficients if the sample is anisotropic. Optical anisotropy exhibits a two-fold symmetry and, therefore, contributes to the $10\omega t$ coefficients for a sample-to-compensator rotation ratio of $5:1$ due to the additional modulation of the $dc$ term. The $2\omega t$ and $4\omega t$ coefficients undergo further modulation as well and contribute to the coefficients $10 \mp 2 = 8, 12$ and $10 \mp 4 = 6, 14$, respectively. Hence, it is necessary to set the synchronization ratio to at least $5:1$ for a rotating-compensator–rotating-sample system in order to avoid distortions of the $2-\omega t$ and $4-\omega t$ coefficients.

Measuring optically induced anisotropy is standard in the surface sciences [6, 7], and is often done in the form of reflection difference spectroscopy (RDS) applied to a wide range of in-situ [8, 9] as well as ex-situ studies of semiconductor surfaces and interfaces. However, while most of these applications are based on normal-incidence...
measurements, equivalent or similar to that introduced by Aspnes [10], our non-normal incidence configuration is mathematically more difficult to handle, since p-polarization needs to be considered in addition to s-polarization.

Rather than deriving analytical expressions for the transmitted anisotropy signal, a numerical simulation is performed, which relates our non-normal incidence anisotropy signal to normal-incidence RDS for thin, anisotropic films on an isotropic substrate. The non-normal incidence equations were derived by Hingerl and Aspnes [11] in the thin film limit, where \( d \ll \lambda \). Although we work in the same limit, our numerical formulation is general.

### 3.1 Theory

Optical anisotropy of a sample leads to mixed polarization states under non-normal-incidence conditions, i.e., the sample matrix \( \tilde{S} \) (Eq. (2.1.4)) has now off-diagonal elements \( \tilde{r}_{ps} \) and \( \tilde{r}_{sp} \) in addition to the diagonal elements, here denoted by \( \tilde{r}_{pp} \) and \( \tilde{r}_{ss} \).

For a thin anisotropic overlayer, the elements of \( \tilde{S} \) are given by

\[
\tilde{r}_{pp} (\theta, \phi) = \tilde{r}_{pp}^o \left( 1 + \frac{4\pi idn_{a\perp}}{\lambda} \frac{\epsilon_s - \epsilon_o - \left( \frac{\epsilon_a}{\epsilon_{s\perp}} - \frac{\epsilon_{s\perp}}{\epsilon_a} \right) \epsilon_a \sin^2 \theta + \Delta \epsilon \frac{n_{a\perp}}{\epsilon_{s\perp}} \cos (2\phi)}{\epsilon_{s\perp} - \epsilon_a} \right),
\]

\[
\tilde{r}_{ss} (\theta, \phi) = \tilde{r}_{ss}^o \left( 1 + \frac{4\pi idn_{a\perp}}{\lambda} \frac{\epsilon_s - \epsilon_o - \Delta \epsilon \cos (2\phi)}{\epsilon_{s\perp} - \epsilon_a} \right),
\]

\[
\tilde{r}_{sp} = -\tilde{r}_{ps} = \frac{4\pi idn_{a\perp}}{\lambda} \left( \frac{n_{a\perp} \Delta \epsilon \sin (2\phi)}{\epsilon_{s\perp} + \epsilon_{a\perp}} \right),
\]

where \( \phi \) is the sample azimuth, \( \theta \) is the angle of incidence, \( \tilde{r}_{pp}^o \) and \( \tilde{r}_{ss}^o \) are the corresponding two-phase expressions for the bare substrate (Eq. (1.4.2)) and \( \epsilon_o = \)
\[(\epsilon_{xx} + \epsilon_{yy})/2 \text{ and } \Delta \epsilon = (\epsilon_{xx} - \epsilon_{yy})/2 \] are the average- and the difference of the in-plane components of the overlayer dielectric tensor, respectively.

To relate non-normal-incidence to normal-incidence measurements, the system matrix is calculated for 25 equally spaced compensator azimuths, where the sample azimuth is synchronized to the compensator by \( \phi = 5C \). The resulting 25 intensity values are Fourier transformed to yield the spectrum of Fourier coefficients, in particular \( \alpha_{10} \) and \( \beta_{10} \).

The computation is carried out for various combinations of polarizer and analyzer azimuths and compared to the normal-incidence RDS signal, which is calculated according to [11] from

\[
\frac{\Delta \tilde{r}}{\tilde{r}} = \frac{\Delta r}{r} + i \Delta \phi = \frac{4\pi id_{n_a} \perp \epsilon_{xx} - \epsilon_{yy}}{\lambda} \frac{\epsilon_s - \epsilon_a}{\epsilon_s - \epsilon_a}.
\] (3.1.2)

### 3.2 Computation

For ease of the argument, we assume hypothetical substrate and ovelayer dielectric functions of \( \epsilon_s, \epsilon_o = 10 + 0i \), respectively. Further, the difference in the planar components of the overlayer dielectric tensor is taken to be \( \Delta \epsilon = 1 + 1i \), and it is assumed that \( \epsilon_{zz} = \epsilon_o \). The computation is carried out for 250 consistently spaced energies from 1.5 to 6.0 eV and compared to the normal-incidence RDS-signal \( \Delta \tilde{r} / \tilde{r} \) obtained from Eq. (3.1.2).

**Normal-incidence, \( P, A = 0^\circ \)**

Figure 3.1 shows the result for \( \theta = 0 \).

This case is of special interest for the following reasons: (1) the normalized 10\( \omega t \)-coefficients are independent of the retardation of the waveplate, since \( dc \rightarrow |r|^2 (3 + \cos \delta) /4 \).
Figure 3.1: The simulated signals $\Delta \tilde{r}$ and $\alpha_{10}$, $\beta_{10}$ for normal incidence for the model described in the text.
and, therefore,

$$\frac{\alpha_{10}}{dc} = \frac{\Delta|r|^2}{|r|^2}.$$  \hspace{1cm} (3.2.1)

Equation (3.2.1) is closely related to the normal-incidence RDS expression, the difference between $\Delta r$ and $\alpha_{10} / dc$ being exactly a factor of 2, which follows from

$$\frac{\alpha_{10}}{dc} = \frac{\Delta rr^*}{rr^*} = \frac{\Delta r^*}{r^*} + \frac{\Delta r}{r} = \frac{2\Delta r}{r};$$  \hspace{1cm} (3.2.2)

from Eq. (3.2.1) it also follows that (2) $\alpha_{10}$ is a real quantity, and that the phase $\Delta \varphi$ is not accessible from the RCE-Fourier coefficients, i.e., we have access to the real part of $\Delta \tilde{r}$ only. The meaning of $P, A = 0$ in the normal-incidence case is that the direction of polarization is aligned with the x-direction of the principal sample axes when $C = 0$. For $P, A \neq 0$ a physically meaningless rotation between the $10 \omega t$ coefficients would be introduced.

**Non-normal incidence, $\theta = 70^\circ$**

The non-normal incidence case where $\theta = 70^\circ$ corresponds to our experimental configuration. It is anticipated that the amplitude of $\alpha_{10}$ is significantly increased over the normal-incidence measurement since the angle of incidence is close to Brewster’s angle for the materials considered here. However, when $P \neq 0$ this advantage is lost because of the large contribution of s-polarized light to the $dc$ term.

Figure 3.2 compares $\alpha_{10}$ and $\beta_{10}$ for $\theta = 0$ and $70^\circ$. In both cases $\beta_{10}$ is zero, but $\alpha_{10}$ is amplified in the $70^\circ$ case by a factor of almost 11. As discussed, this is expected for materials where $\theta$ is close to Brewster’s angle, i.e., where $|r_p|^2$ in the denominator of Eq. (3.2.1) becomes small. For the hypothetical model considered
Figure 3.2: At $\theta = 70^\circ$ $\alpha_{10}$ is amplified by a factor of almost 11 compared to normal incidence for the model described in text. $\beta_{10}$ is zero in both cases.

here, $\theta_B = 72.5^\circ$.

Figure 3.3 compares the $10 \omega t$ coefficients obtained at normal incidence to $\theta = 70^\circ$; in both cases $P = -30^\circ$ and $A = 0$. Obviously, $\alpha_{10}$ is diminished to a magnitude comparable to the normal-incidence signal, which is a result of the contribution from the s-polarized component. The curvature in the graphs where $\theta = 70^\circ$ follows from the dispersion of the $MgF_2$ waveplate. Actual values from the experimental configuration were used for the retardation $\delta$. In contrast, $\alpha_{10}$ and $\beta_{10}$ in Fig. 3.2 were calculated assuming a wavelength-independent retardation of $\pi/4$. Note that, as above, the
Figure 3.3: Comparison of $10 \omega_t$ coefficients for typical deposition conditions where $P, A = -30^\circ, 0^\circ$, and for $\theta = 0, 70^\circ$ for the model described in text.

signal is always independent of the retardation for normal-incidence measurements. $P = -30^\circ, A = 0^\circ$ corresponds to typical conditions for data acquisition and, therefore, this case establishes important information for interpreting our data correctly.

For completeness, the cases where $P = \mp 45^\circ$ and $A = \pm 45^\circ$ are evaluated as well. Figures 3.4 and 3.5 show the corresponding results.

To conclude this chapter, non-normal-incidence anisotropy measurements can be made more sensitive then normal-incidence measurements when only p-polarized light
Figure 3.4: Comparison of $10 \omega t$ coefficients for $P, A = -45^\circ, 45^\circ$ for $\theta = 0, 70^\circ$ for the model described in text.
Figure 3.5: Similar to Fig. 3.4, but for $P, A = 45^\circ, -45^\circ$. 
is used, which improves the signal-to-noise ratio as discussed in [11]. However, in order to simultaneously measure the reflectance-difference signal and the pseudo dielectric function both p- and s-polarized light is needed and, hence, the signal-to-noise ratio is comparable to that of normal-incidence RDS.

The dispersion of the compensator retardation leads to additional complications by introducing a purely instrument-dependent curvature in the $10\omega t$-coefficients under non-normal-incidence conditions.

For all practical non-zero polarizer azimuths, the amplitudes of non-normal-incidence measurements are comparable in magnitude to the normal-incidence case. The line-shapes are distorted due to compensator dispersion, which must be considered on a case-by-case basis. The results obtained here should be sufficient to allow the spectra obtained to be discussed qualitatively under typical deposition conditions.
Chapter 4

Experimental Configuration

The overall purpose of this research project is to obtain time-resolved information about OMCVD processes with an optical in-situ probe that monitors the state of a sample during all stages of epitaxial growth. In particular, our RCE configuration simultaneously measures the pseudo-dielectric function, which returns information about the bulk material, and the reflectance difference signal, which for isotropic layers and substrates is sensitive to surface-induced optical anisotropy.

The configuration (Fig. 4.1) employs a single optical beam reflected from a rotating sample. Spectra from 230 to 840 nm are obtained at repetition rates of up to 5 per second with a resolution of 1024 pixels. During one rotation of the compensator the diode array is scanned 25 times in equally spaced intervals. Discrete Fourier analysis yields the first twelve harmonics of the detected signal, where the coefficients $\alpha_0, \ldots, \beta_4$ are related to $|r'_p|^2$, $|r'_s|^2$, and $r'_p r''_s^*$ as discussed in Ch. 2. By synchronizing the spindle rotation to the compensator rotation at a ratio of 5 : 1, sample induced optical anisotropy is detected in the $10 \omega t$ coefficients.
Figure 4.1: Basic configuration of the integrated system.
4.1 Advantages of a rotating disk reactor

For in-situ work it is important that a rotating disk reactor can be equipped with window ports for optical access to the growth interface. In our system the windows are located relatively far away from the substrate and are purged with carrier gas, so that deposition on the windows is avoided. The two additional ports do not appear to cause distortions of the main gas flow pattern.

Forced gas flow (pumping) due to the spinning sample generates a highly stable and reliable gas flow pattern over the sample. Since the gases are redirected radially outward, there is virtually no intermixing of reacted and un-reacted precursor materials up-stream of the sample. Therefore, it is possible to precisely define and control chemical reaction boundary layers.

The cylindrical symmetry of the reactor simplifies the mathematical description for hydrodynamic flow inside the reactor. In the special case of a rotating disk with infinite radius and a semi-infinite homogeneous ambient, the problem of gas flow in three dimensions, as described by the Navier-Stokes equations [12], is reduced to a one-dimensional boundary value problem by means of the von Karman similarity transformation. The discussion of gas flow dynamics by Breiland et al. is based on this transformation applied to a rotating disk reactor. The theoretical results can be used as approximate starting values to determine the flow settings for a reactor with a finite-sized disk.

From an optical-diagnostics perspective, the major advantage of a rotating-disc reactor is that it allows us to access surface chemistry by sample anisotropy. The anisotropy here arises almost entirely from dimers on the growth surface with their
characteristic spectral dependencies. However, to obtain useful results with an ellip-
someter it is essential that the rotation of the sample is synchronized to the rotation
of the appropriate element of the ellipsometer, as previously shown by us for the RPE
[13]. This eliminates rotating sample reactor designs such as that used by Aixtron,
where the sample rotation is achieved by vanes on the sample mount that cause an
essentially uncontrolled rotation that depends on gas-flow conditions.

4.2 Modified Emcore GS 3300 OMCVD reactor

Research was carried out on a modified Emcore GS-3300 OMCVD system. This
station was originally designed for simultaneous processing of three 3” wafers, but was
refitted in the past with a smaller 6” reactor for processing of single 2” wafers. This
redesigned reactor includes two opposing 70° ports for optical access to the sample
near Brewster’s angle. The ports are terminated with strain-free quartz windows
(suprasil) that are mounted on neoprene o-ring seals.

The original rotating sample stage was replaced with a unique spindle design for
dynamic runout control of the spinning substrate. This functionality is achieved
through a mechanical adjustment mechanism that is controlled by two external, rota-
tion decoupled micrometer screws, which allow the sample to be tilted in two orthog-
onal directions relative to the spindle shaft while the spindle is rotating. This on-line
adjustment capability is essential for optical in-situ diagnostics on a rotating sample:
if the reflected beam exhibits wobble, the signal is distorted due to the additional
modulation of the detected intensity. We found it impossible to mount the sample
relative to the sample holder in such a way that additional adjustments may be omit-
ted. The sample tends to shift its position during spin-up, and during the heating
and cool-down phases of the substrate. My main contribution here, which proved to be necessary to obtain more accurate data, was to replace the original ball-and-socket pivot, which was unstable at high temperatures, with a rocking-disk design that is stable under all conditions. This is described in Sec. 4.3.

As discussed briefly above, the reactor is of the vertical-flow-turbo-disk type, with the carrier gas/precursor mixture injected through the top flange. The gases are pumped downward towards the growth interface by means of a concentration gradient as well as the viscous drag of the rapidly spinning substrate. Typical rotation rates are 900 to 1600 $rpm$, depending on the net gas flux through the reactor, as well as the substrate temperature. The injection system consists of a specialized top flange with integrated, flow-balanced injector nozzles. The flange is designed to create three concentric flow regimes, the outermost of which contains pure carrier gas and the middle and center regions inject the carrier gas plus precursor mixture. Prior to injection the gases in each region are forced through a fine stainless steel mesh to create a homogeneous flow pattern. The pure carrier gas in the outermost ring provides a curtain of inert gas that prevents heterolytic reactions of precursor molecules with the stainless steel reactor wall. The inner two regions are supplied with a mixture of carrier gas and precursors. Their relative flow rates can be adjusted to minimize radial deposition gradients, i.e., to promote a constant film thickness over the sample.

Initially the gas flow direction is straight down from the top flange. However, due to the viscosity of the atmosphere inside the reactor, and as a consequence of the spinning sample and sample holder, the flow pattern picks up increasing radial and circumferential velocity components with decreasing distance to the sample, i.e., the gases flow in a spiraling motion towards the spinning disk. The hydrodynamics of a
4.3 Rotating spindle with dynamic run-out control

Figure 4.2 shows a technical drawing of the specialized spindle shaft. The shaft consists of three sections. (1) The top part holds the molybdenum arbor that supports the susceptor, the sample holder, and the sample. Welded into the bottom of the arbor mount is the control (wobble-) stick. Welding ensures a rigid connection between the two pieces such that they remain parallel. (2) The lower part is a hollow stainless steel shaft, that houses the control stick and supports the arbor rotating disk reactor of this type are reviewed in an article by Breiland et al. [14].

Finally, all gases exit the reactor and flow into the exhaust system. The exhaust configuration includes a back-streaming filter, a particle filter, a pneumatic shut-off valve to isolate the reactor, a butterfly throttle valve, to control the reactor pressure, a scrubber to neutralize hazardous gases, and finally an exhaust into the building stack.
piece. (3) The third part contacts pairs of bearing balls, one pair of which are silver soldered into opposing, spherical bore-outs in the top face of the hollow shaft and the second pair similarly to the bottom face of the arbor piece. Each set of receptacles consists of a spherical bore-out to lock one ball, and a u-shaped groove in which the second ball can slide in and out. The combination of spherical bore-out and u-shaped groove forms a geometric clamp that locks the rocking ring into place but allows for differential heat expansion of the individual pieces. The two sets of receptacles make a $90^\circ$ angle so that the arbor can be tilted relative to the shaft in any direction.

The wobble stick passes through the hollow shaft and the rocking disk, and is tapered to ensure maximum rigidity while retaining the maximum range of motion.

At the bottom end of the control stick is a stainless steel block, which is locked into position by a combination of a pair of ball and lever assembly and return springs (not drawn). The two levers are perpendicular to each other so that the block can be positioned anywhere within the range of the wobble stick. Each of the levers pushes vertically upward a stainless steel ball that travels in a $45^\circ$ race, translating upward/downward motion to sideways motion of the block. The levers are manipulated by two concentric pushrods that rotate with the spindle. The forces that act on the pushrods are supplied by stationary micrometer screws and translated onto the pushrods by thrust bearings that decouple the rotation from the micrometer screws. The sample tilt is adjusted with the micrometer screws while the spindle is rotating, so that the sample normal can be aligned at any time without interrupting growth.

The geometry of the assembly determines the available range in tilt angle. The inner diameter of the hollow shaft is 0.625”, the diameter of the lower end of the wobble stick is 0.25”, and the distance from the lower end of the hollow shaft to the
pivot point is 15”. The resulting maximum range for adjusting the sample is ±0.71°. Technical drawings of the components are included in appendix B.

The runout (wobble) of the sample is continuously monitored by reflecting a Helium-Neon laser beam from the sample surface and projecting the spot onto a screen 5 m from the sample. A typical value for sample wobble at 1200 rpm for an aligned sample is 0.03°.

This design has proven to be stable for temperatures of up to 1000°C and for rotation rates in excess of 1500 rpm.
Chapter 5

Calibration of the Integrated RCE System

As with any optical instrument, the integrated RCE configuration requires alignment and calibration. An alignment step is necessary each time a sample is loaded into the reactor and/or when the setup has been disturbed in any way. Alignment of a rotating-compensator system is considerably more complicated than that of a rotating-analyzer or -polarizer system, since more parameters need to be determined. Moreover, the accuracy needed when reflectances as well as complex reflectance ratios are analyzed requires extra care in correcting for stray light and overlap of orders on the spectrometer. In particular we develop a new approach to determine and correct artifacts due to diffraction in second- and third-order.

First, the plane of incidence needs to be defined by aligning the sample orientation with the axis of rotation of the rotational sample stage (spindle). This step establishes a frame of reference for subsequent measurements as well as the zero reference for all (optical) components of the RCE spectrometer. Due to residual imbalances in the spindle, the axis of rotation tends to shift as the rotational speed increases. Therefore, calibration begins only after the sample has been brought up to speed and is rotating
under deposition conditions.

Sample run-out (deviation of the sample normal with respect to the axis of rotation) is monitored continuously with a laser as described in Ch. 3. After the initial alignment, additional re-alignment steps are necessary when the sample settles to a new equilibrium position under changing conditions. In particular, re-settling occurs during spin-up of the sample and during temperature changes. While the spindle was extremely stable after it was initially fabricated, it became increasingly unstable over two years, and finally required service.\textsuperscript{1} In any case, our experience has shown that some type of real-time adjustment capability is essential for optical monitoring. I also emphasize that our mechanical solution, however complex, provides the needed range of motion while it functions reliably over a wide range of rotational speeds (0-2000 rpm), temperature (RT - 1000\(^\circ\)C), and reactor pressures (atmospheric - to the terminal 22 mTorr of our pump). This spindle is truly unique in its capability to provide real-time positioning of the sample.

We next consider calibration of the optical components. Here, the reactor pressure is set to the target growth pressure of the experiment to follow so the possibility of contributions due to pressure changes and dependencies is ruled out. Calibration is done in the following sequence: (1) polarizer azimuth, (2) analyzer azimuth, (3) compensator azimuth, (4) compensator dispersion, (5) wavelength calibration, (6) correction for higher-order artifacts. Azimuth calibration consists of finding the laboratory frame that corresponds to their being aligned with the plane of incidence.

Compensator dispersion deals with the determination of the retardation of the magnesium fluoride monoplate as a function of pixel number of the array detector.\textsuperscript{1}

\textsuperscript{1}The source for the instability actually turned out to be a screw connection, which was too weak to lock the susceptor to the rotating spindle and wore out over time.
Wavelength calibration establishes the correspondence between pixel number and wavelength. Higher-order artifacts refer to multiple wavelengths arriving at a given pixel as a result of higher-order diffraction by the grating. These are discussed in the following section. Related and alternative alignment procedures are discussed in the literature in particular in references [15, 16, 17, 18].

5.1 Polarizer calibration

The first step in my calibration procedure is to find the azimuth angle of the polarizer that corresponds to the polarization vector lying in the plane of incidence. The rotational stage of the polarizer has a resolution of 0.01°, which is the (mechanical) limit to the accuracy to which the plane of incidence can be determined. In the procedure I take advantage of the parallel-processing capability of the photodiode array, as will become clear in the following.

When the polarizer is aligned with the plane of incidence, and only $p-$ polarized light is incident on the sample, the substrate acts simply as a mirror. Even though the compensator offset is not known at this stage, it is possible to find the zero offset of the polarizer by taking the ratio of the $4C$ coefficients $\beta_4/\alpha_4$. The equation describing this ratio is

$$\frac{\beta_4}{\alpha_4} = \frac{\left(|\vec{r}'_p|^2 - |\vec{r}'_s|^2\right) \sin (4C - 2A) + (\vec{r}'_p \vec{r}'_s^* + \vec{r}'_p^* \vec{r}'_s) \cos (4C - 2A)}{\left(|\vec{r}'_p|^2 - |\vec{r}'_s|^2\right) \cos (4C - 2A) - (\vec{r}'_p \vec{r}'_s^* + \vec{r}'_p^* \vec{r}'_s) \sin (4C - 2A)}$$

where as before $\vec{r}'_p = \vec{r}_p \cos P$ and $\vec{r}'_s = \vec{r}_s \sin P$. As $P$ approaches zero, the coefficient $(\vec{r}'_p \vec{r}'_s^* + \vec{r}'_p^* \vec{r}'_s)$ vanishes, and the factor $\left(|\vec{r}'_p|^2 - |\vec{r}'_s|^2\right)$ cancels. Accordingly, $\beta_4/\alpha_4$ becomes independent of the sample properties. Since the readout delay between
pixels is constant, when \( P = 0 \) the phase increases linearly with diode number, providing a condition that allows \( P = 0 \) to identified. At the same time the values of \( \tan^{-1}(\beta_4/\alpha_4) \) yield the correction phases that must be applied to each pixel. Thus, the polarizer and phase-reference for the compensator are determined simultaneously.

Figure 5.1: Values of the merit function \( \chi^2(P) \) as a function of \( P \) for a range of values of \( P \) about the plane of incidence. The apex of the fitted parabola coincides with \( P = 0.06^\circ \) in this calibration run.

To provide a measure for the best linearity I step the polarizer through a total range of 1.0° with the plane of incidence lying approximately halfway between the extremes. I then fit \( \tan^{-1}(\beta_4/\alpha_4) \) to a straight line and record the values of the merit
function

$$\chi^2(P) = \sum_{i=1}^{1024} \left( (\text{linear fit})_{i} - \tan^{-1}(\alpha_{i}/\beta_{i})_{i} \right)^2$$  \hspace{1cm} (5.1.2)

for each sampling point \(P\). The set of pairs \((P, \chi^2(P))\) obtained from this procedure establishes the goodness of fit as a function of polarizer azimuth. The merit function \(\chi^2\) exhibits a parabolic dependence on \(P\) with a minimum at \(P = 0\).

Typical results for the parabolic dependence and the best-fit straight lines are shown in Figs. 5.1 and 5.2, respectively. The minimum of \(\chi^2\) occurs at \(P = 0.06^\circ\) with a probable uncertainty of less than \(0.02^\circ\). The best-fit straight line is shown in Fig. 5.2, along with results where \(P\) deviates from the plane of incidence by \(\pm 0.5^\circ\). It can be appreciated that this procedure is possible only because the whole spectral range is measured simultaneously, which allows me to use the wavelength as an additional dimension.

Fig. 5.2 shows that the straight-line dependence fails for pixel numbers higher than about 600 for this sample, in this case GaAs. The reason is that in energy ranges where the sample is absorbing the slightly elliptically polarized modes of the quartz Rochon prisms interact to first order with the sample, which means that Eq. (5.1.1) is not quite accurate under these conditions. The onset of absorption in GaAs is indicated by the arrow in Fig. 5.2. Accordingly, these modes are independent of the polarizer azimuth. The pixel range for all fits is 125 to 600, which corresponds to a wavelength range of 780 to 481 nm, respectively. Choosing a range for fitting is somewhat ambiguous, so the resulting values for offset and slope of the straight line should be viewed as a first approximation. Never the less, this procedure determines the plane of incidence to within \(0.02^\circ\) with a reproducibility of about \(0.01^\circ\).
Figure 5.2: $\tan^{-1}(\beta_4/\alpha_4)$ at $P = 0$, as determined by minimizing the residual in a best-fit straight line for $n < 600$. Inset: $\tan^{-1}(\beta_4/\alpha_4)$ for $P = \pm 0.5^\circ$.

Even though these numbers represent typical values, they should be used with care because the accuracy of the polarizer calibration results depends on how well sample wobble can be eliminated. For instance, if the sample is warped, or its runout is larger than usual, it is in principle not possible to define a stationary plane of incidence, and the polarizer calibration routine can only be a "guesstimate" of the average location of the plane of incidence. In practice our spindle runs sufficiently accurately so this is not a problem. Also, substrates do not usually exhibit warpage if they have not been used before. In general we obtain very satisfactory results with
the above procedure, even though one has to deal with a spinning sample inside a closed reactor, each of which could be a source of serious complications.

Figure 5.3: Expanded view of the graphs in figure 5.2 for the long wavelength end of the spectrum. Distortions due to diffraction into higher orders are present when $P \neq 0$ but vanish when the polarization vector is parallel to the plane of incidence ($P = 0$).

As an interesting detail, distortions in $\tan^{-1}\left(\frac{d\alpha}{d\beta}\right)$ due to the effects of higher order diffraction cancel out of the ratio when $P = 0$. In contrast, for $P \neq 0$ they affect the data, predominantly in the long wavelength range, as shown in Fig. 5.1. Higher order diffraction is actually beneficial to this calibration procedure, since it increases the sensitivity of $\chi^2$. 
5.2 Analyzer calibration

Determining the reference azimuth for the analyzer poses a special difficulty for an RCE in the Polarizer-Sample-Compensator-Analyzer (PCSA) configuration. This is due to the fact that the system is referenced to \((4C - 2A)\) for the coefficients \(\alpha_4\) and \(\beta_4\) and \((2C - 2A)\), for the coefficients \(\alpha_2\) and \(\beta_2\), respectively. From the Fourier coefficients, it is not possible to distinguish between a compensator offset \(C_\infty\) (Sec. 5.3) and the analyzer azimuth \(A\). As an additional complication, the compensator phase calibration discussed in the next section yields the phase offset \(C_\infty\) only if the analyzer is oriented parallel to the plane of incidence. Since the plane of incidence may change whenever a new sample is loaded, the azimuths of compensator and analyzer must be redetermined before a measurement can be performed. In other words, it is not possible to establish a universal, sample-independent reference that can be used in general.

My solution to this problem is somewhat unusual and requires a system modification (i.e., thinking outside the RCE box). I determine the analyzer reference azimuth by removing the compensator, which leaves the system in the polarizer-sample-analyzer configuration. In this case the transmitted intensity is given by Eq. (5.2.1). For accuracy, the effects of optical activity of the polarizer and analyzer have been included.

\[
I = \left|\tilde{r}_p\right|^2 \cos^2 A \cos^2 P + \left|\tilde{r}_s\right|^2 \sin^2 A \cos^2 P \\
+ \frac{1}{2} Re (\tilde{r}_p \tilde{r}_s^*) \sin 2A \sin 2P \\
- \frac{1}{2} Im (\tilde{r}_p \tilde{r}_s^*) (-\gamma_p \sin 2A + \gamma_a \cos 2P) \\
+ O(\gamma_a^2, \gamma_p^2, \gamma_a \gamma_p)
\]
Apart from the effects of optical activity, Eq. (5.2.1) indicates that $I$ has two extrema: for $P = 0^\circ$ or $90^\circ$ (1) a maximum when the polarizer and the analyzer prisms are parallel, and (2) a minimum when the prisms are crossed. To align the analyzer, I use the minimum condition where $P = 90^\circ$ and $A = 0$. For this configuration, Eq. (5.2.1) simplifies to

$$I = |r_s|^2 \sin^2 2A + Im(\bar{r}_p r_s^*) (i\gamma_p \sin 2A + i\gamma_a).$$  

(5.2.2)

Figure 5.4: Transmitted intensity as a function of analyzer azimuth. $P = 90^\circ$.

For small angles $A$, Eq. (5.2.2) reduces to a polynomial of second degree. Figure 5.4
shows $I$ as a function of $A$ together with a parabolic fit for the same GaAs sample used in Figs. 5.1 and 5.2. For each channel of the diode array a similar curve is obtained.

The condition for the minimum is

$$\frac{dI}{dA} = \frac{1}{4} |r_s|^2 \sin 2A + 2\gamma_a Im (\tilde{r}_p \tilde{r}_s^*) \cos 2A = 0 \quad (5.2.3)$$

whence

$$\tan 2A = -\frac{8\gamma_a Im (\tilde{r}_p \tilde{r}_s^*)}{|r_s|^2}. \quad (5.2.4)$$

In figure 5.4, the position of the minimum for each channel is shown as a function of energy. Since $\gamma_a \approx 0.0010 (E/eV)$ [19, 20] in the region where the sample is transparent the azimuthal angle at which the minimum occurs scales approximately linearly with energy. Thus the analyzer offset can be established by extrapolating a linear fit to the data of Fig. 5.5 to $E = 0$.

It is worthwhile to point out that this method of eliminating the effects of optical activity is only possible because the whole spectrum is recorded in parallel so that again the wavelength is used as an additional dimension. In principle, one could obtain the same information with scanning technology, but this is usually not done, probably because the calibration time multiplies according to the number of sampled wavelengths and thus becomes unreasonably long.

### 5.3 Compensator calibration

The polarizer calibration routine yields two pieces of information. One is the polarizer azimuth and the other is the value $(4C - 2A)$. The fact that the phase reference
Figure 5.5: Minima of the fitted intensity curves as a function of energy. The influence of optical activity increases linearly with energy.

can be found for each pixel of the diode array has some interesting and very useful implications.

First, it needs to be understood that readout of the entire PDA proceeds one pixel at a time at a rate of 5 $\mu$s/pixel. Thus, the time required to scan the entire array is 5.12 ms. Since the compensator is rotating, each diode readout occurs at a different compensator azimuth, which means that the phase $(4C - 2A)$ will be different for each of the 1024 channels. This behavior is evidenced by the slope of the data in Fig.
5.2. $C$ itself is composed of four different contributions:

$$C = \omega_c t + C_{oo} + C_{o,i} + C_{o,\tau},$$  \hspace{1cm} (5.3.1)

where $\omega_c$ is the rate of rotation of the compensator, $C_{oo}$ is the actual offset of the compensator principle axis that is used for referencing from the plane of incidence, $C_{o,i}$ is the compensator offset as a function of diode number, which is established by the readout speed of the diode array and the rate of rotation of the compensator, and $C_{o,\tau}$ are offsets due to any delays that are introduced by the system’s electronic components. I.e., there is a time delay between the generation of a trigger pulse by the encoder and the actual onset of the corresponding array scan. In practice, $C_{oo}$ and $C_{o,\tau}$ are added together and treated as one effective compensator offset, which I subsequently refer to as $C_{oo}$. The delays $C_{o,\tau}$ make it essentially impossible to align the compensator statically and then analyze the data obtained with the compensator rotating continuously.

5.3.1 Compensator phase correction

The system is aligned when $A = P = 0$, the compensator offset $C$ is known for each pixel, and the coefficients $\alpha_4$, $\beta_4$, $\alpha_2$, and $\beta_2$ are rotated back to the $C = 0$ plane. If the system is aligned certain symmetries should be observed. For example Eq. (2.1.13) shows that for the crossed polarizer configurations $(P, A) = (\mp 45^\circ, \pm 45^\circ, 45^\circ)$ the coefficients are either identical or the inverses of one another. I use this symmetry to obtain an estimate of the accuracy of the calibration routines.

Figure 5.6 shows typical Fourier coefficients for the two crossed polarizer configurations of the calibrated system. The coefficients resemble each other closely but obviously they do not match exactly. For viewing purposes only the $\alpha_4$ coefficients
are plotted in Fig. 5.7, and their difference in given in the inset. Figure 5.8 also shows the relative difference between the two graphs, which is 5 to 10% depending on wavelength. Since the polarizer and analyzer prisms have been aligned, the discrepancy must be attributed to an uncertainty in the compensator-phase of Eq. (5.1.1). This is not surprising, since the linear fit to \( \tan^{-1}(\beta_4/\alpha_4) \) is affected by optical activity where the sample is absorbing\(^2\), which leaves us with an ambiguity in \((4C' - 2A)\). Thus determination of the compensator offset from Eq. (5.1.1) is a first assessment and it is possible to make some improvements. Further, alignment of the optical components is critical for simultaneously determining the overlayer parameters \( n \), \( k \) and \( d \), so I developed and implemented the correction procedure that is discussed in the next section.

**Improved phase correction**

The coefficients \( \alpha_4 \) and \( \beta_4 \) are given by

\[
\begin{align*}
\alpha_4 &= \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |\tilde{r}'_p| \right)^2 - |\tilde{r}'_s| \right]^2 \cos 2A - 2Re \left( \tilde{r}'_p \tilde{r}'_s^* \right) \sin 2A \\
\beta_4 &= \frac{1}{2} \sin^2 \left( \frac{\delta}{2} \right) \left[ \left( |\tilde{r}'_p| \right)^2 - |\tilde{r}'_s| \right]^2 \cos 2A + 2Re \left( \tilde{r}'_p \tilde{r}'_s^* \right) \sin 2A
\end{align*}
\] (5.3.2)

I suppose that the compensator principal axes do not line up exactly with the plane of incidence but are offset by a small angle \( \delta \). In that case \( \alpha_4 \) and \( \beta_4 \) are rotated into each other so that \( \cos 2A \) is actually \( \cos (2A + \delta) \) and \( \sin 2A \) is \( \sin (2A + \delta) \). These functions can be rewritten as

\(^2\)In this case the sample is Silicon, where the absorption threshold occurs for \( n \geq 700 \) in contrast to Gallium Arsenide (\( n \geq 600 \)).
Figure 5.6: Coefficients $\alpha_2/\alpha_0, \ldots, \beta_4/\alpha_0$ after the initial calibration for the two crossed polarizer configurations $A = \pm 45^\circ, P = \mp 45^\circ$.

\[
\begin{align*}
\cos 2A + \delta &= \cos 2A \cos \delta - \sin 2A \sin \delta \tag{5.3.3} \\
\sin 2A + \delta &= \sin 2A \cos \delta + \cos 2A \sin \delta. \tag{5.3.4}
\end{align*}
\]

With polarizer and analyzer crossed at $A = 45^\circ$ and $P = -45^\circ$ the ratio of $\alpha_4/\beta_4$ takes on the following simple form:

\[
 r_- \equiv \left( \frac{\alpha_4}{\beta_4} \right)_{P=-45, A=+45} = \frac{-k_1 \sin \delta + k_2 \cos \delta}{k_1 \cos \delta + k_2 \sin \delta}, \tag{5.3.5}
\]
Figure 5.7: $\alpha_4$ coefficients for polarizer and analyzer in the two crossed configurations.

$$r_+ \equiv \left( \frac{\alpha_4}{\beta_4} \right)_{P=+45^\circ, A=-45^\circ} = \frac{k_1 \sin \delta + k_2 \cos \delta}{-k_1 \cos \delta + k_2 \sin \delta}, \quad (5.3.6)$$

where $k_1 = (|\tilde{r}_p|^2 - |\tilde{r}_s|^2)$ and $k_2 = (\tilde{r}_p\tilde{r}_s^* + \tilde{r}_p^*\tilde{r}_s) = 2Re(r_p r_s^*)$. Since $\delta$ is assumed to be small $r_+ \text{ and } r_-$ can be expanded to first order in $\delta$. The sum $r_+ + r_-$ becomes

$$r_+ + r_- \simeq \frac{k_1 \delta + k_2}{-k_1 + k_2 \delta} + \frac{k_1 \delta + k_2}{k_1 + k_2 \delta} = \frac{2\delta (k_1^2 + k_2^2)}{-k_1^2 + k_2^2 \delta^2}, \quad (5.3.7)$$

Also, the quantity $1 - r_+ r_-$ becomes

$$1 - r_+ r_- = \frac{(k_1^2 + k_2^2)(-1 + \delta^2)}{-k_1^2 + k_2^2 \delta^2}. \quad (5.3.8)$$
Figure 5.8: Relative difference $\Delta \alpha_4/\alpha_4$ for $P = \pm 45^\circ$ and $A = \mp 45^\circ$.

Equations (5.3.7) and (5.3.8) can be combined into one ratio to yield

$$\frac{r_+ + r_-}{1 - r_+ r_-} = \frac{2\delta (k_1^2 + k_2^2)}{(k_1^2 + k_2^2)(-1 + \delta^2)} = -2\delta + O(\delta^2). \quad (5.3.9)$$

Equation (5.3.9) is very convenient and useful because it can be identified with the inverse tangent relationship

$$\tan^{-1} r_+ + \tan^{-1} r_- = \frac{r_+ + r_-}{1 - r_+ r_-}. \quad (5.3.10)$$
Therefore

\[
\frac{1}{2} (\tan^{-1} r_+ + \tan^{-1} r_-) = -\delta. \tag{5.3.11}
\]

Equation (5.3.11) states that the phase offset \(\delta\) for each pixel of the diode array can be determined by measuring \(\alpha_4/\beta_4\) for the two configurations for which polarizer and analyzer are crossed. In general, the resulting value for \(\delta\) is a linear function of pixel number. Its offset is the correction to \(C_{oo}\) and its slope is the correction to \(C_{oi}\).

Figure 5.9: Phase correction applied to \(\alpha_4\).

Figure 5.9 shows the effect of the phase correction on the \(\alpha_4\) coefficient. Here,
\( \alpha_4 \) was measured in the two crossed polarizer and analyzer configurations. Again, the two curves should coincide. As shown in the inset, the difference between the two curves is now of the order \( 10^{-4} \) or better in the transparent region and becomes appreciable only in the absorbing region of the spectrum. Compared to the difference in \( \alpha_4 \) when the phase correction is not applied, the improvement a factor 100. The residual discrepancy can now be attributed to system limitations, such as the accuracy to which polarizer and analyzer can be positioned.

For diode numbers higher than 750 the uncorrected values for \( \alpha_4 \) start to separate. In this region the sample, Silicon in this case, becomes absorbing and generates circular polarized light. These circular components couple to the optical activity of the quartz-Rochon prisms, which results in a contribution to \( k'_1 \). To first order in \( \gamma_a \), \( k'_1 \) becomes

\[
s_1 = 2\text{Re}(\tilde{r}_p\tilde{r}_s^*) - 2\gamma_a\text{Im}(\tilde{r}_p\tilde{r}_s^*). \tag{5.3.12}
\]

Clearly, the correction procedure does not apply for this region of the spectrum.
5.4 Optical activity

5.4.1 Introduction

I denote one section to optical activity of the crystalline quartz prisms, because this phenomenon affects the calibration and data acquisition, and must also be considered when discussing the $\Delta R/R$ approach to solving simultaneously for the three unknown overlayer parameters $Re(\epsilon_o)$, $Im(\epsilon_o)$, and $d$.

The structure of $\alpha-$quartz used in Rochon prisms is helical and, therefore, rotates the direction of polarization of the electric field vector. Right-handed (positive-) and left-handed (negative-) crystalline quartz exists in nature with a specific rotation of $\rho = \pm 3.8 \text{ rad/cm}$ at $\lambda = 589.3 nm$ [21]. To verify the calibration routines, I determine the effect of optical activity on the polarizer- and analyzer calibration, and on the compensator retardation. I calculate the outcome in the presence- and absence of optical activity and then analyze the difference.

All computations are based on model calculations, using the dielectric function of Gallium Arsenide,\(^3\) and assuming that the coefficients for optical activity depend on energy as $\gamma = 0.001 (E/eV)$.

5.4.2 Effect on the polarizer calibration

At the time of the polarizer calibration the analyzer azimuth is not known. Figure 5.10 shows the values for $\tan^{-1}(\beta_4/\alpha_4)$ for different values of the polarizer azimuth in the absence of optical activity. I use an arbitrary analyzer offset of $0.2^\circ$, since this is of the order of a typical offset after a new sample has been installed. The curves are symmetric about $A$ and the calibration routine, which is based on minimizing $\chi^2$

\(^3\)D. E. Aspnes and A. A. Studna Physics Rev.
Figure 5.10: Polarizer calibration in the absence of optical activity. Shown are curves for \( \tan^{-1} \left( \frac{\beta_4}{\alpha_4} \right) \) for \( 0.10^\circ \leq P \leq 0.10^\circ \).
Figure 5.11: Curvature in $\tan^{-1} \left( \frac{\alpha_4}{\alpha_4} \right)$ due to optical activity for $-0.15^\circ \leq P \leq 0.10^\circ$.

of the fit to a straight line, will converge to $P = 0$.

In the presence of optical activity Fig. 5.11 shows the resulting values for $\tan^{-1} \frac{\alpha_4}{\alpha_4}$. Also drawn are the linear fits for the transparent region. The curves are so longer symmetric about $P = 0$ but exhibit an added negative curvature for all values of $P$. Furthermore, the offset of the $P = 0$ curve corresponds to a value of $A = 0.25^\circ$ when measured by the intersection of the $P = 0$ curve with the $y$ axis. The best linear fit, i.e., where $\chi^2$ is a minimum no longer occurs at $P = 0$, but rather at $P = -0.075^\circ$, as shown in Fig. 5.12. Thus, if optical activity is ignored, the polarizer calibration
5.4.3 Effect on the analyzer calibration

The analyzer azimuth is determined with the compensator removed from the RCE, i.e., in the PSA configuration.

Figure 5.13 shows the residual transmitted intensity for $P = 90^\circ$ and $A = 0^\circ$. The intensity is zero for ideal elements (black curve). The red and green curve show the contribution from the analyzer and the polarizer, respectively. The blue curve is the combined effect from both elements. Fig. 5.14 shows the resulting intensity as a function of the analyzer azimuth at $1.5\, eV$. The apex of the parabolic fit is at $-0.001^\circ$, which corresponds to the analyzer offset due to optical activity. This offset is smaller than the resolution of the stepping motor, which positions the analyzer prism, and can be viewed as negligible. This is in support of the idea that optical activity effects can be removed by extrapolating the minima of Fig. 5.5 to $E = 0$. In practice it is sufficient to use minimum at $1.5\, eV$.

In summary, the effects of optical activity on the analyzer calibration routine can be made, essentially, zero, when the long wavelength end of the available spectrum is used for the calibration.

5.4.4 Effect on compensator retardation

Figure 5.15 shows the deviation of the measured retardation from its true value as result of optical activity in the polarizer and analyzer prisms. For this plot I calculated the coefficients $\alpha_0$ and $\alpha_4$ assuming an initial retardation of $\pi/4$ for all wavelengths then including $\gamma_a$ and $\gamma_p$ in the computation. The apparent retardation was then determined from $\alpha_4/\alpha_0$ at $P = A = 0$, using the relationship
Figure 5.12: $\chi^2(P)$ considering the effects of optical activity. The minimum is shifted by $0.075^\circ$ compared to the ideal case of Fig. 5.10.
Figure 5.13: Transmitted intensity for crossed polarizers. Black: ideal prisms, red: residual due to the analyzer, green: residual due to the polarizer, blue: combined effect of analyzer and polarizer.
Figure 5.14: Transmitted intensity as a function of the analyzer azimuth near $A = 0$. The distortion of the analyzer calibration due to optical activity is about 0.001° at 1.5 eV.
Figure 5.15: Distortion of the measured values of the compensator retardation due to optical activity of the quartz-prisms of polarizer and analyzer, respectively.
\[
\cos \delta = \frac{1 - 3 \frac{\alpha_4}{\alpha_0}}{1 + \frac{\alpha_4}{\alpha_0}},
\]

(5.4.1)

where \(\delta\) is the retardation retardation of the wave plate. The difference between the input values for \(\delta\) and the apparent values is shown in figure 5.15 as a function of energy, is everywhere less than 0.01°.

While this value is relatively small, it is large enough to influence the outcome of certain analysis procedures, for instance that of the \(\Delta R/R\) method, to be discussed in Sec. 6.3.
5.5 Diffraction into higher Orders

5.5.1 Introduction

Along with the speed advantage due to the parallel-processing capability of PDA detectors comes the disadvantages of having to deal with diffraction of light in second and third orders. This phenomenon is inherent in optical diffraction gratings and causes distortions of the detected signal over a wide range of pixels. For instance, our CP-200 detector employs a holographic reflection grating with a line spacing of $5 \times 10^{-3} \text{ mm}$ (or 200 lines/mm). As a result, there are signal contributions from second-order diffraction in pixels 1 through 600, which corresponds to 860 to 480 nm first-order diffraction, and 430 to 240 nm second-order diffraction. The mixing of the spectroscopic information in these two wavelength ranges constitutes the single largest systematic error in this application. Third order diffraction is also present, but it affects only diodes 1 through 280, with corresponding wavelengths of 860 to 680 nm in first order, and 287 to 227 nm in third order. In this region there is overlap of first-, second-, and third orders of diffraction.

5.5.2 The effect of higher order contributions on the detected signal

Figure 5.16 shows the transmitted intensity for a quasi-monochromatic input line of $\lambda = 253 \text{ nm}$. Second and third order of diffraction occurs at twice and three times the fundamental wavelength, respectively. Depending on the wavelength, the fraction of intensity that is channelled into second and third orders in our system is $2 - 10\%$ and $0 - 3\%$, respectively.

Figure 5.17 shows the effect of higher orders of diffraction on the measured Fourier
Figure 5.16: The response of our detector to a quasi-monochromatic input of $\lambda = 253\,\text{nm}$.

coefficients. The arrows indicate the onsets of second- and third- order diffraction, respectively. Also shown are coefficients where the contributions from higher orders have been removed by the procedure to be discussed. From figure 5.17 it is obvious that the phenomenon causes a serious distortion of the signal in the region where most semiconductors are transparent. However, the transparent region is of particular interest here, because it allows us to extract the overlayer thickness from the optical signal by means of interference between waves reflected from the substrate-overlayer and overlayer-ambient interface, respectively. Furthermore, the transparent region is
Figure 5.17: The effect of higher-order diffraction on the normalized Fourier coefficients \( \alpha_2/\alpha_0, \ldots, \beta_4/\alpha_0 \) for a Silicon sample. The arrows indicate the onset of second-order- and third-order-diffraction, respectively.

also where the RCE is most superior to the RPE, since the phase \( \Delta \) is close to 180° in this region. Whence, there is sufficient interest to reclaim the transparent region of the spectrum for useful data analysis by removing the contributions from higher order diffraction.

5.5.3 Removing higher order artifacts by filtering

Since the advantages of parallel processing are so drastically degraded by higher-order diffraction – basically rendering the obtained data useless for serious analysis – it was
necessary to explore methods of removing higher-order contributions. One common approach is to use optical bandpass filters, that reject the short wavelengths that overlap in second and third order with the long wavelengths detected in first order. While this method is probably the most accurate one, it reduces acquisition rates by at least a factor of two, since spectra need to be obtained with and without the filter. This means developing a sophisticated mechanism for inserting and removing the filter in the beam. Since the time constants for certain reactions are of the order of 0.1 s, e.g., for reconstruction changes, a significant reduction of the acquisition rate is not acceptable.

A second approach is to place a series of filters directly onto the PDA [22, 15, 23]. While this methods dos not reduce the acquisition rate, it is somewhat cumbersome at causes artifacts at the locations where different filters are joined. Furthermore, there is a chance of damage to the pixel array during the mounting process. Finally, filters will always reduce the signal due to reflections at the front and back surfaces even in their region of nominal transparency. Since the light levels are generally low at the extremes of the available spectrum, increased noise levels must be anticipated here.

Everything considered, I discard filters as an optical for removing higher order artifacts in this application. The same considerations may apply to other high-speed, broad band systems.

5.5.4 Numerical correction of higher-order artifacts

Having rejected the filtering option I next consider the possibility of correcting the data post-acquisition. The method is feasible for the following reasons. In consider first the Poynting vector [4]
\[ \vec{S} = \frac{c}{4\pi} \left( \vec{E} \times \vec{H} \right), \tag{5.5.1} \]

that describes the intensity of an electromagnetic field. Since the intensity has many spectral components I write

\[ \vec{E} = \int_{-\infty}^{+\infty} d\omega \vec{E}'(\omega) \ e^{-i\omega t} \]
\[ \vec{H} = \int_{-\infty}^{+\infty} d\omega \vec{H}'(\omega) \ e^{-i\omega t} \tag{5.5.2} \]

The PDA responds to intensity integrated over the dwell time \( \tau \) of the pixels. This can be written

\[ \varepsilon = \int_A dr^2 \int_{-\tau/2}^{\tau/2} dt \int_{-\infty}^{+\infty} d\omega d\omega' \vec{E}'(\omega) \cdot \vec{E}^* (\omega') \ e^{-i(\omega+\omega')t}, \tag{5.5.3} \]

where \( A \) is the area of a given pixel. Performing the time integration gives

\[ \varepsilon = \int_A dr^2 \int_{-\infty}^{+\infty} d\omega d\omega' \vec{E}'(\omega) \cdot \vec{E}^* (\omega') \frac{\sin \left( \frac{(\omega-\omega') \tau}{2} \right)}{\frac{\tau}{2} (\omega - \omega')} \tag{5.5.4} \]

The term \( \frac{\sin (\omega-\omega')\tau/2}{(\omega-\omega')\tau/2} \) is the \( \text{sinc} \) function, which is plotted as \( \text{sinc} (x) \) in Fig. 5.18.

The envelope of \( \text{sinc} (x) \) falls off as \( 1/x \) and is appreciably different from zero only for reasonably small arguments. As an example, I consider a typical dwell time \( \tau = 5 \text{ ms} \) at \( \lambda = 600 \text{ nm} \) (\( \omega = 3.14 \times 10^{15} \frac{\text{rad}}{s} \)). Then \( 1/x \approx 6 \times 10^{-14} \). More to the point, even for frequencies close to 600 nm the \( \text{sinc} \)-function behaves as a \( \delta \)-function, so the \( \omega' \) integration can be performed trivially. The net result is that we may add these quantities as intensities, and in particular higher orders overlapping lower orders.
Accordingly, it is possible to numerically correct the distorted spectra by simply subtracting the signal contributions due to second- and third-order diffraction. Implementation of this procedure requires that we know the contributions from higher orders for every pixel. Further, the contributions need to be determined self-consistently every time a spectrum is acquired. The following paragraph describes in more detail...
the correction method that I have implemented to accomplish this.

5.5.5 Implementation of higher order correction

The challenge here is to determine the higher-order contributions for each pixel. The procedure must be self-consistent, i.e., it must work for varying light levels. Therefore, no single universal correction will work. However, if I can establish the relative distribution of intensity into the different orders then the correction values can be obtained from the intensity of the fundamental wavelength and the appropriate scaling factors. This requires in turn two pieces of information: the relationships among first-, second-, and third-order pixel numbers, and the scaling factors for the fraction of intensity channelled into the higher orders relative to the first-order intensity. This relative intensity distribution is also a function of wavelength.

I first tried to determine the relative intensity distribution by measuring the transfer function of the detector with continuously tuneable quasi-monochromatic light from a Cary 14 monochromator. This required the detector to be removed from the RCE. I found it possible to determine the general behavior of the transfer function, but it became clear that the result depends on relative positioning of the detector in the beam path. I thus decided to obtain these data with the detector in place using a set of narrow bandpass filters, which also allow the pixels to calibrated according to the positions of the first, second, and third order diffraction peaks. An example of the three detected orders of diffraction resulting from a $\lambda = 239 \text{ nm}$ filter is shown in Fig. 5.16. Since the pixel-wavelength relationship is linear only a relatively small number of measurements are needed. Fig. 5.19 shows the relative position of first-, second-, and third-order diffraction peaks as determined with five narrow bandpass filters.
To obtain the relative intensity distribution I two measurements with the RCE. I first determine the values of the distorted coefficients $\frac{\alpha_2}{\alpha_0}$, $\frac{\beta_2}{\alpha_0}$, $\frac{\alpha_4}{\alpha_0}$, and $\frac{\beta_4}{\alpha_0}$ for a polarize azimuth $P \neq 0$, such that $\alpha_2$ and $\beta_2$ are not equal to zero. Next, I introduce a filter into the path, that is opaque for short wavelengths so that no second- or third-order contributions are present. The choice of filter is such that the cutoff occurs as closely as possible to the wavelength where second-order effects begin (Corning A3-72 is used here). This yields relative-intensity coefficients $\gamma_{12}$ and $\gamma_{13}$ for second- and third-order diffraction, respectively. These vary slowly enough with $\lambda$ that they may be fit by low order polynomials. The analytic expression used in Fig. 5.20 is actually
\[ P_1 + \frac{P_2}{(P_3 - x)}, \] where \( x \) corresponds to pixel number in the discrete case. I am using this function to extrapolate the \( \gamma_{12} \) to pixel numbers \( n < 225 \), where second- and third-orders overlap. Since I have not enough information to separate the \( \gamma_{12} \) from the \( \gamma_{13} \) it is necessary to fix one in order to find the other. The function that I use extrapolates without oscillations and is therefore save to use for establishing the values \( \gamma_{12} \) in this region.

Having determined the \( \gamma_{12} \) as a function of pixel number, it is now straight forward to correct the various coefficients according to

\[
\begin{align*}
dc(i_2) & \rightarrow dc(i_2) - \gamma_{12}(i_2) dc(i_1), \\
\alpha_2(i_2) & \rightarrow \alpha_2(i_2) - \gamma_{12}(i_2) \alpha_2(i_1), \\
\beta_2(i_2) & \rightarrow \beta_2(i_2) - \gamma_{12}(i_2) \beta_2(i_1), \\
\alpha_4(i_2) & \rightarrow \alpha_4(i_2) - \gamma_{12}(i_2) \alpha_4(i_1), \\
\beta_4(i_2) & \rightarrow \beta_4(i_2) - \gamma_{12}(i_2) \beta_4(i_1),
\end{align*}
\]

where \( i_1 \) is the pixel that coincides with the first-order peak, and \( i_2 \) is the pixel where the second-order replica occurs.

The values for \( \gamma_{13} \) are obtained similarly but on coefficients that have been corrected for second-order effects.

Figure 5.17 shows the result of the higher-order correction procedure applied to the normalized Fourier coefficients. The corrected coefficients are smooth functions of wavelength, which indicates that the obtained values are related to the actual physical properties of the material rather than to artifacts of the detector.

One critical assessment of the correction procedure is to look at its effect on the \( dc \)– instead of the normalized coefficients. In figure 5.21 I show the transmitted
Figure 5.20: The relative weights $\gamma_{12}$ as a function of pixel number. Also shown is an analytic representation.
intensity for the quasi-monochromatic line of \(\lambda = 253.7 \text{ nm}\). On the bottom is the intensity distribution measured without corrections. At the top is the corrected \(dc-\) \((\alpha_0)\) coefficient. The second- and third-order artifacts have vanished on the scale of the figure, leaving the spectrum nominally flat in this region. Apart from a slight overcorrection, this is the desired intensity distribution for my application.

Figure 5.21: Numerically-corrected and uncorrected intensity- \((dc-)\) values for the 253.7 \(nm\) line of Hg.

For comparison and completeness, the effect on the \(dc\) coefficients for wavelengths \(\lambda = 239 \text{ nm}, 253 \text{ nm}, 300 \text{ nm}, \) and \(360 \text{ nm}\) is shown in Figs. 5.22 and 5.23. The individual spectra have been scaled to the height of their first-order diffraction peaks,
respectively. To better visualize the slight overcorrection, all spectra are offset from zero by 10%.

There are four types of improvements, that might be made to the procedure implemented here. (1) The corrections could be done as a function of energy, which would give better resolution at high energies and yields symmetric lineshapes of the diffracted peaks. (2) A larger number of narrow-band pass filters would provide a more accurate diode relationship between the different orders of diffraction, better taking into account the slightly non-linear relationship between the pixel number and λ. (3) Use of $\alpha_2$ and $\beta_4$ in addition to $\beta_2$ and $\alpha_4$ to improve the values obtained for $\gamma_{12}$ and $\gamma_{13}$. Nevertheless, I have shown that a relatively simple numerical (as opposed to mechanical) procedure solves the problem of diffraction into higher orders. Since this does not reduce the rate at which full spectral information is obtained, it will be especially useful for high-speed, broad-band applications. The procedure implemented here is the first of its kind and should be viewed as prototypical.
Figure 5.22: Uncorrected $d_c$—coefficient for filters cvi239, O253, cvi300, and cvi360, respectively.

Figure 5.23: As figure 5.22 but numerically corrected.
5.6 Spectral calibration

I calibrated the pixel array with a Hg/Ar spectral calibration lamp.

Figure 5.24 shows the detected intensity as a function of wavelength. The 253.7 nm line is present in first-, second- and third order. The 365.0 nm and 404.6 nm lines generate noticeable second-order but no third-order peaks. Wavelengths from ref. [24] are indicated in parenthesis. The result is shown in Fig. 5.25.

The uncertainty in wavelength is about 1.5 nm at pixel 1 and increases to about 3 nm for pixel 1024.
Figure 5.25: Wavelength calibrated pixel array.
Chapter 6

Extraction of overlayer information

6.1 Introduction

When a film is deposited on a substrate, the reflection coefficients $\tilde{r}_p$ and $\tilde{r}_s$ change as a function of the overlayer parameters $n$, $k$, and $d$, where $\tilde{n} = n + ik$ is the complex index of refraction of the overlayer and $d$ is the layer thickness.

Of particular interest is whether it possible to use $|r_p|^2$, $|r_s|^2$, and $\tilde{r}_p\tilde{r}_s^*$ to extract $n$, $k$, and $d$ from the data and thus to establish the dielectric properties of the depositing film, especially on a thickness scale of the order of Ångstroms. If so, optical probes would be ideally suited for sample driven, closed loop feedback control of deposition processes, and many properties of scientific and technological interest would be available for study. A general method for directly extracting all three parameters from optical data is a problem that has been investigated for at least 30 years, and a general solution is long wanted.

In this chapter I discuss two approaches that, in principle, can yield the three parameters, even though it is safe to say that there is no straightforward, general solution to the problem. In large, this is due to the fact that the overlayer information is smoothed out due to mixing with the optical response from the substrate.
The problem is of the inverse type in the sense that we know the response of the system from our measurement yet would like to reconstruct the sample structure and properties from the measured data. The analysis of inverse problems is closely related to the so-called Fredholm integral equation of the first kind [25], where a response kernel, i.e., the model that is used to describe the sample, is integrated over the sampling space, e.g., the penetration depth of light, to produce the detected signal. The topic is studied widely in the literature with an entire journal *Inverse Problems* devoted to this and related issues.

For the analysis of experimental data, the integral equation needs to be discretized, here into stratified layers, where each layer contributes to the overall signal. As pointed out by Aspnes [26], and also by Power [27], if the thickness of the individual layer becomes too thin, the solution becomes necessarily unstable, because the response from adjacent layers is increasingly correlated. This is the main reason why Fresnel-analysis of multiple layers fails if the thickness increments are chosen too small.

Imaging applications are also based on the inversion of a system kernel, where one would like to extract as much structural information as possible about the source from a (limited) knowledge of the far-field radiation pattern [28, 29]. This is relatively straightforward in situations where the wavelength is much shorter than the typical dimension of the object, but it becomes a particularly difficult task in situations where the size of the object is comparable to the wavelength [30, 31]. To better appreciate the overlayer problem, note that the wavelength we use to probe the three-phase structure is about 5000× greater than the thickness of the film, which is the reason why optical diagnostics of thin films is in fact a daunting task.

However, inversion of the three-phase model is not an inverse problem in the same
sense as the inversion of a Fredholm integral equation: (1) in a Fredholm type inversion one seeks to reconstruct the profile of a single quantity, e.g., the concentration of impurities as a function of depth due to ion implantation [32, 17], or the normal velocity distribution on the surface of a sound source [30], whereas the inversion of the three-phase model requires that three independent quantities be determined and, consequently, (2) that a system of three coupled equations be solved simultaneously. (3) In inverse problems, spectral information is typically used to increase the number of data points, where spatial features are independent of wavelength. However, in our case the index of refraction is a function of wavelength, which means that the problem must be solved independently for each wavelength.

There are also major differences between ellipsometry/polarimetry and imaging: (1) in imaging it is typical to measure the intensity distribution without discriminating between different states of polarization. In polarimetry we determine not only the overall intensity, but also the distribution into p- and s- polarization, as well as the relative phase between p- and s-waves. This constitutes three pieces of information instead of one. (2) We do not detect the spatial distribution of the intensity, since reflection by the sample is considered to be specular.

### 6.2 Methods discussed

The particular methods discussed are (1) the so-called $\Delta R/R$ approach, which is also known as “three parameter ellipsometry” [33], and which was proposed by Paik et al. in 1971 [34], and (2) a variation to lineshape analysis, which is my own development, and which is possible because of the spectral capabilities of our instrument.
The $\Delta R/R$ method uses a differential measurement of the pseudo-dielectric function $\Delta <\epsilon>$ (actually $\Delta \psi$ and $\Delta \Delta$) in combination with a differential measurement of the power reflectance $\Delta R_p/R_p$, where $R_p = |r_p|^2$, to solve the resulting system of three equations for the three unknown overlayer parameters on a wavelength-by-wavelength basis. Since we have access to these quantities, it seemed logical to analyze our data by employing the $\Delta R/R$ approach.

However, we encountered unexpected difficulties with this method, which initiated a closer investigation into its mathematical foundation, which has not been done so far. In particular, the solution behaves erratically and tends to diverge without obvious reasons. As it turns out, the system of equations that needs to be inverted is nearly singular, which is a consequence of the weak sensitivity of s-polarized light to the presence of an overlayer and the functional similarity between the p- and s-power-reflectances. Consequently, the numerical degree of independence becomes vanishingly small, which perpetuates a “catastrophic” dependence of the extracted overlayer parameters on small errors in the data. A formal solution is guaranteed, however, by the fact that $R_p$ and $R_s$ are non-analytic functions. As shown in appendix C, two analytic functions cannot be combined to yield three independent, analytic functions. A result that is probably not surprising.

(2) The second approach is based on lineshape analysis. The new feature here is that the overlayer dielectric function is represented by a low-order polynomial to establish an analytic representation of the spectral dependence in the transparent region. For an underlying substrate that requires higher-order terms in a Taylor series expansion it is possible then to distinguish between the overlayer and the pseudo-substrate by finding the thickness that minimizes the figure-of-merit function $\chi^2$ of
the low-order-polynomial (parabolic) fit.

Even though the requirements for this approach seem somewhat artificial, the method has proven to generate results where no assumptions were made about the depositing film for thicknesses as small as one (1) Ångstrom. In particular, the method has been used to determine the thickness and dielectric function of excess Ga deposited during a reconstruction experiment on GaAs, and to extract a 1 Å thickness increment of a growing GaAs film on an AlGaAs pseudosubstrate.

This approach therefore goes beyond the exponential spiral approximation [35], where overlayer information is obtained from the trajectory of \(<\epsilon>\) in the complex plane. The exponential spiral method requires knowledge of either the deposition rate (thickness), or the curvature of the trajectory, i.e., the second derivative of \(<\epsilon>\) with respect to thickness, and is therefore limited not only by noise, since the derivatives need to be taken of the data, but also by the fact that at least three data points are needed to establish curvature information. Accordingly, as pointed out in reference [36], a layer thickness greater than 20 Å is typically needed, which is far too much considering the currently required thickness resolution of the order of Ångstroms. However, the exponential spiral approach is the only one to date that has demonstrated sample driven closed-loop feedback control of OMCVD deposition processes for growth of compositionally graded structures [37].

6.3 The \(\Delta R/R\) Approach

The changes \(\Delta <\epsilon>\) and \(\Delta R/R\) are equated to the corresponding expressions obtained in the three-phase model, and the resulting system of transcendental equations
is solved numerically on a wavelength-by-wavelength basis for \( n, k, \) and \( d \). The discussion is traditionally formulated in terms of the ellipsometric angles \( \psi \) and \( \Delta \) [38], where \( \tilde{\rho} = \tilde{r}_p / \tilde{r}_s = \tan \psi \ e^{i\Delta} \). However, the quantities returned by the RCE are \( |r_p|^2 \), \( |r_s|^2 \) and \( \tilde{r}_p \tilde{r}_s^{*} \), as discussed in Sec. 2.1.3. Accordingly, the discussion here is based on these quantities rather than ellipsometric angles whose meaning is merely of historical value in the context of RCE systems.

The broadband capability of our configuration also requires an investigation of the spectral dependence of the method, which has been applied in the past to reversible electrochemical processes at a relatively small number of single wavelengths.

While several authors have claimed to determine overlayer parameters successfully, the results are not readily convincing [34, 39]. Therefore, we perform model calculations to (1) understand the behavior of the solution and (2) to establish the requirements on accuracy and precision of the RCE spectrometer in order to establish the system requirements for the equations to be solved to an acceptable level of accuracy. Further, since the solution depends on the particular combination of materials, (3) it is necessary to perform a separate analysis for each material system that is being studied.

### 6.3.1 Problem statement

Mathematically the problem can be formulated in the following way: find the vector \( \vec{x} = (n, k, d) \) that solves the system of equations

\[
\vec{F} (\vec{x}) = \vec{f} (\vec{x})_{\text{model}} - \vec{f}_{\text{exp}} = 0, \tag{6.3.1}
\]

where \( \vec{f} = (Re (\tilde{r}_{p,s}^{*}) , Im (\tilde{r}_{p,s}^{*}) , |r_{p}^{*}|^2) \) and \( \vec{f}_{\text{exp}} \) are the corresponding experimental values. \( \vec{f}_{\text{model}} \) represents the solution of the Fresnel equations in the three-phase
model. In principle the results can be applied to more complicated configurations by using the common-pseudosubstrate approximation [40, 41], but we do not investigate this extension here. In the three-phase model $r_p' r_s^* r_p' \star$ and $|r_p'|^2$ depend on $n$, $k$, and $d$, or equivalently $\epsilon_\alpha$ and $d$, through $r_{\alpha a}$, $r_{s o}$, and $Z = e^{2ikn_o z d}$ (Eq. 1.4.1). Obviously, the system of equations is transcendental, since the product $n_{o, z} d$ enters through the argument of the phase term $Z$. Thus, in practice the solution must be obtained numerically. This is done, for instance, with a Newton-Raphson routine, which uses a first-order expansion of the three-phase model to obtain a linearized system of equations, which is then solved by matrix inversion. From the perspective of a current set of parameters $\bar{x}_0$, the linearized system is given by

$$\bar{F}(\bar{x}_0 + \delta \bar{x}) = \bar{F}(\bar{x}_0) + \bar{J}\delta \bar{x} = 0,$$

(6.3.2)

where it is assumed that $\bar{x}_0 + \delta \bar{x}$ solves Eq. (6.3.1). $\bar{J}$ is the Jacobian matrix, whose elements $J_{ij}$ are the derivatives $\partial F_j / \partial x_i$ of the components of $\bar{F}$. The corrections $\delta \bar{x}$ are obtained from the inverse matrix $\bar{J}^{-1}$, whose properties determine the behavior of the solution.

The model calculations are carried out using a three-phase system consisting of 5 Å of GaP on a GaAs substrate. The values for $\epsilon_s$ and $\epsilon_\alpha$ were obtained from ellipsometric measurements of bulk material at room temperature [42]. The angle of incidence is 70°, which coincides with that of our RCE.

Figure 6.1 shows the obtained determinant $\text{DET} (\bar{J})$ as a function of energy. Zero crossings at 3.26 eV, 4.13 eV, and 5.15 eV indicate that the system becomes independent of at least one of the three parameters at these points. The singularity at 4.13 eV is anticipated, since it coincides with an isoplectic point, where the addition
Figure 6.1: The determinant of the Jacobian as a function of energy for a 5 Å layer of GaP on GaAs at $\theta = 70^\circ$. Zero crossings are indicated by arrows.
or the removal of overlayer material does not lead to a change in the pseudo-dielectric function, i.e., the system becomes independent of \( d \).

It is instructive to look at the positive and negative terms of the determinant. The two curves combined and the determinant, which is the difference between them, is shown in Fig. 6.2. The near singularity of the system is evidenced by this graph. The positive and negative contributions are virtually identical with the resulting determinant diminished by two to three orders in magnitude. As mentioned above, the small determinant indicates that the solution is unstable, where small errors in the data lead to large uncertainties in the determined values of \( n \), \( k \), and \( d \).

This approach has been used occasionally in the electrochemical community. The near-singularity-characteristic most likely explains why it has not become a standard experimental technique for determining the three overlayer parameters. It also explains the wide scatter in the extracted values of \( n \) and \( k \) in results published by Horkans et al. [39], and Cahan states that, "Intuitive reasoning (with the help of experience) provides a procedure for finding all the roots." [33]. As I show here, it is actually the fundamental nature of the problem that makes data analysis so challenging.

### 6.3.2 Model Calculation

To investigate this further, I apply the procedure to simulated data as above for 5 Å GaP on GaAs at an angle of incidence of 70°. The functions \( f_1 \), \( f_2 \), and \( f_3 \) are given by
Figure 6.2: The determinant of the Jacobian (DET), and its positive- (DETP) and negative- (DETM) constituents for the model described in the text.
\[ \vec{f} = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \end{pmatrix} = \frac{1}{s_0} \begin{pmatrix} \Delta |r_p|^2 \\ 2 \text{Re} \left( \Delta \tilde{r}_p \tilde{r}^*_p \right) \\ 2 \text{Im} \left( \Delta \tilde{r}_p \tilde{r}^*_p \right) \end{pmatrix} \]

(6.3.3)

where the differences are taken between the substrate + overlayer and the bare substrate, respectively. The \( f_i \) are normalized to the intensity \( s_0 \) of the substrate to remove the artificial dependence on the light source. Figure 6.3 shows the energy dependence of the simulated functions. A double precision Newton-Raphson routine has been used to solve for \( \epsilon_o \) and \( d \), where \( \epsilon_o = (n + ik)^2 \) is the equivalent of \( n_o \) and \( k_o \). The results are shown in Figs. 6.4 and 6.5, respectively, and the difference between the input and extracted overlayer dielectric function \( \epsilon_o \) is shown in Fig. 6.6.

The divergencies at 3.26 eV, 4.13 eV, and 5.15 eV are expected, since the determinant of \( \tilde{J} \) crosses zero at these points. The deviations in the transparent region are an indication of a loss in sensitivity here as well.

As a final piece of supporting evidence Fig. 6.7 shows the eigenvalues of \( \tilde{J} \) for 250 consistently spaced energy values in the same spectral range (1.5 to 6.0 eV). One of the three eigenvalues is diminished by four orders in magnitude (\( \approx 1 \times 10^{-6} \)), compared to the other two. A zero eigenvalues means that the system of equations is linearly dependent. The numerical degree of independence for the three-phase system is vanishingly small.

### 6.3.3 Dependence on the angle of incidence

Figure 6.8 shows the dependence of the 3.61 eV maximum of \( DET(\tilde{J}) \) on the angle of incidence. The highest sensitivity is expected for \( \theta = 71.6^\circ \) for this material system, which is very close to the experimental setting of 70°. Hence, it is not possible to improve the approach by changing to a different angle of incidence.
Figure 6.3: $\Delta R_p/R_p$ and $\Delta r_p r_s^*$ constitute the functions $f_1$, $f_2$, and $f_3$, here for 5 Å of GaP on a GaAs at an angle of incidence of 70°.
Figure 6.4: The extracted overlayer dielectric function $\varepsilon_o$ for a 5 Å layer of GaP on GaAs, as described in the text.
Figure 6.5: The extracted overlayer thickness $d$ for a $5\,\text{Å}$ GaP layer on GaAs, as described in the text.
Figure 6.6: Differences between input and extracted values of $\epsilon_o$ for 5 Å GaP on GaAs, as described in the text.
Figure 6.7: Eigenvalues of the Jacobian in the ΔR/R approach.
Figure 6.8: Dependence of $\text{DET}(\hat{J})$ on the angle of incidence for the model described in the text. Maximum sensitivity can be expected at $71.7^\circ$, in our experiment the angle of incidence is $70^\circ$. 
6.3.4 Error propagation and system requirements

Due to the near singularity of the Jacobian, it is necessary to take a close look at the effect of experimental uncertainties on the derived values for $\epsilon_o$ and $d$. I consider two sources of errors, which are (1) statistical noise of the measurement, and (2) systematic errors due to uncertainties in the system parameters of the RCE.

**Statistical noise**

The uncertainties from statistical noise are determined by the inverted Jacobian and the standard deviations $\sigma_{f_i}$ of the observables $f_i$, which are obtained from

$$\sigma_{x_i}^2 = \sum_{j=1}^{3} (J^{-1}_{ij})^2 (\sigma_{f_j})^2,$$

where $\sigma_{x_i}$ is the variation in $x_i$, and $\vec{x} = (\epsilon_{o,r}, \epsilon_{o,i}, d)^T$, as above.

The values for the standard deviations $\sigma_{f_i}$ were calculated from 1024 repetitive measurements of the Stokes parameters with the sample rotating at 1200 rpm and at a reactor pressure of 60 Torr, i.e., under typical deposition conditions. However, the quantities that are used for $\Delta R/R$ approach are normalized differences in the form of $\frac{\Delta s_i}{s_0}$, which cannot be measured repetitively without interrupting growth. Therefore, the standard deviations of $\frac{s_i}{s_0}$, $i = 1, 2, 3$ are used as estimates for the $\sigma_{f_i}$, which are obtained according to

$$\sigma_{f_i} \approx \sqrt{\frac{1}{N-1} \sum_{j}^N \left( \frac{s_i}{s_0} \right)_j - \left( \frac{s_i}{s_0} \right)}^2.$$  

(6.3.5)

In principle, the $\sigma_{f_i}$ need to be evaluated separately for each pixel, however, the pixel-to-pixel variations are essentially negligible here, so that a common value for all pixels can be assumed. Further, the three $\sigma_{f_i}$ are of the same order of magnitude, so
that estimating the associated uncertainties in $\epsilon_o$ and $d$ can be done by assuming a common value for all of them. From analyzing several pixels of the spectral range, I find that a value of $5 \times 10^{-4}$ represents the statistical fluctuations $\sigma_f$.

Figure 6.9 shows the resulting uncertainties for the extracted values of the over-layer dielectric function. The statistical uncertainties are generally greater than the values themselves by one to two orders in magnitude, which is in accord with the diminished determinant of the Jacobian. In our experiment, statistical noise would need to be reduced by at least to two three orders of magnitude for the resulting
uncertainties to fall within the percentile range. This is not possible with present technology.

Implications for the electrochemical experiments also follow. Since these are generally done on similar materials, similar conclusions should apply. That is, for the $\Delta R/R$ approach to work, statistical uncertainties would have to be reduced to the $10^{-6}$ range. This is marginally possible with modulation techniques, explaining the somewhat erratic level of success of the experiments.

**System parameters**

The second source for error is the uncertainty in the system parameters of the RCE. The azimuthal angles for the analyzer, the polarizer, and the compensator are calibrated with respective uncertainties of $\approx 0.01^\circ$. In addition to that, uncertainties are associated with the retardation of the waveplate and the angle of incidence.

The angle of incidence and the polarizer azimuth enter this calculation only indirectly through the values for the substrate dielectric function. I assume, however, that $\epsilon_s$ is known accurately, even though this is not the case if it was measured with the same instrument. Here, my focus is on the effects from inaccurate knowledge of the analyzer azimuth and the compensator retardation.

The machine returns a set of observables $f_{i,exp}$ corresponding to the actual system settings of the RCE. The residual $\delta \vec{F} = \vec{f}_{exp} - \vec{f}_{model}$, which results from inaccurate system parameters entering the model calculation, multiplies the inverse Jacobian and generates a correction term $\delta \vec{x}$ to the actual value $\vec{x}$ according to

$$\delta \vec{x} = \tilde{J}^{-1}\delta \vec{F}.$$  \hfill (6.3.6)

First, the analyzer is considered. Figures 6.10 and 6.11 show the corrections to the
overlayer dielectric function and the thickness, respectively, for a deviation of 0.01° in the analyzer azimuth. The true values of $\epsilon_o$ are those of Fig. 6.4, less the errors plotted in 6.6, which are not a result of inaccurate system parameters.

Interestingly, in the transparent region the effect is smaller than in the region where the sample becomes absorbing. The absolute error in $\epsilon_o$ below 3 eV is about 0.1 and 0.025 for the real and imaginary part, respectively. The thickness deviates from the actual value by 3 to 20% in this range.
Figure 6.11: As in Fig. 6.10, but for $d$. 
Next the corrections $\delta \vec{x}$ due to errors in the compensator retardation are considered. Optical activity of the quartz prisms, for instance, affects the measured compensator retardation by distortions up to 0.01° (Sec. 5.4.4). This is viewed as a typical value for the uncertainty in the compensator retardation, but we recognize that the actual uncertainty is energy dependent.

As before, the transparent region exhibits the least sensitivity to this system parameter. The deviations at 1.7 $eV$ are 0.01 and 0.003 for the real- and the imaginary part of $\epsilon_o$, respectively, and 0.1% for the thickness.
Figure 6.13: As Fig. 6.12, but for $\delta d$. 
The existence of spectral regions of low sensitivity to statistical and systematic errors together with a spectral capability suggests one possible way around these problems. Since the thickness is a system invariant, if it is possible to determine \(d\) from data taken over even a small spectral range it should be possible to obtain \(\epsilon_o\) with a much lower level of uncertainty.

### 6.3.5 Results

In my attempts to apply this approach the data from various growth runs, I could not obtain satisfactory results. Besides isolated instances where the values for \(\epsilon_o\) and \(d\) seemed reasonable in parts of the spectrum, predominantly the transparent region, which is consistent with the discussion above, the overall behavior of the solution was highly erratic and the obtained values could not be used to establish the overlayer parameters with confidence.

We also investigated the effects of using ellipsomtric angles \(\psi, \Delta\) instead of the normalized Stokes parameters \(\Delta s_2/s_0\) and \(\Delta s_3/s_0\), and pseudo-dielectric function values \(\Delta \epsilon\) in place of ellipsometric angles. However, these quantities are equivalent, since they are all related to the real and the imaginary part of \(r_p r^*_s\) combined with a normalization to intensity in some form.

In Figs. 6.14 and 6.15 the measured values for \(\Delta < \epsilon >\) and \(\Delta R_p/R_p\) are compared to exact model calculations for which the solution exists. The pseudosubstrate is an AlGaAs structure and the overlayer is GaAs. It was possible to make model calculations in this case because the values for \(\epsilon_o\) were obtained during growth of a GaAs buffer-layer. The thickness is approximately 10 \(\AA\).

The two curves show that the RCE is sensitive to \(\Delta R/R\) for both, \(p\)- and \(s\)-polarized light. The discrepancies between the model and the experiment are
Figure 6.14: $\Delta < \epsilon >$: measured values and model calculation.
too large to apply the $\Delta R/R$ method. The conditions can be improved by further reducing the noise in the system, however, the noise level needed is out of reach with present technology.

### 6.4 Automated lineshape analysis

When the deposition rate (film thickness) is known the overlayer dielectric function can be obtained from a differential measurement of the pseudo-dielectric function alone. If the value for $d$ is chosen greater or smaller than the actual layer thickness,
Figure 6.16: Extracted overlayer dielectric function (GaAs) for 5 Å of GaAs on the AlGaAs-structure of Fig. 6.17. Features reminiscent of the substrate are present when $d$ is chosen too small (curve 2) or too large (curve 3), but not when $d$ coincides with the actual overlayer thickness (curve 1).

the spectrum of $\epsilon_o$ exhibits features reminiscent of the underlying substrate [43].

Figure 6.16 shows the extracted values $\epsilon_o$ for 5 Å of GaAs on the AlGaAs pseudosubstrate shown in Fig. 6.17. As before, the values for $\epsilon_o$ were obtained during growth of the GaAs buffer layer. The pseudo-dielectric function is that of the later grown GaAs/AlGaAs structure. For the correct choice $d = 0.5\, nm$, the input and return values for $\epsilon_o$ are equal (curve1). If $d$ is chosen to be too small or too large, residual features of the underlying substrate are present in the obtained values for $\epsilon_o$. 
For the correct value of $d$, $\epsilon_o$ is a slowly varying function of $\lambda$ (pixel number), which allows me to represent the real and the imaginary part of the overlayer dielectric function with low-order polynomials for pixels 50 to 500. In contrast, for thicknesses that are too large or too small a low-order polynomial cannot reproduce the additional structure from the underlying substrate. In the least squares sense, a "good" representation corresponds to a minimum in the merit function $\chi^2$, whereas a
“poor” representation increases $\chi^2$. The task is to find the thickness which coincides with the minimum in $\chi^2$.

In practice, I pick a lower- and an upper limit to the thickness and advance $d$ in equally spaced increments through this range. The overlayer dielectric function obtained at each thickness is fitted to a parabola and the resulting value for $\chi^2$ is recorded as a function of $d$. At its minimum, $\chi^2$ varies approximately as a quadratic, so that the apex of a parabola fitted to $\chi^2$ as a function of $d$, actually, for true linearity $1/d$, yields the physical layer thickness.

The pixel range for fitting depends on the substrate/overlayer combination. In the case of GaAs on AlGaAs, the transparent region of the individual materials is too similar to be distinguishable by a low-order polynomial. However, the method depends on the behavior of the pseudosubstrate rather than the actual substrate, which implies that a sufficiently thick contrast layer, typically of the order of $10^2 \text{ nm}$, ensures that interference oscillations in the pseudosubstrate provide the necessary structure in the transparent region.

As an example, Fig. 6.18 shows the values of the resulting merit function for 100 thickness increments. About 190 $\text{Å}$ of AlAs were deposited. The corresponding dielectric function is given in Fig. 6.19. The minimum in $\chi^2$ is decisive and can be detected easily. The procedure works also for ultrathin layers. I show in Fig. 6.20 the extracted dielectric function for a 1 $\text{Å}$ thickness increment during the deposition of a GaAs layer on the pseudo substrate of Fig. 6.17. Additional applications of this method are the subject of Ch. 6.

The advantages of this method are (1) that $\chi^2$ establishes a quantitative criterion for the correct choice of $d$, which increases the accuracy by which the thickness can
Figure 6.18: $\chi^2$ as a function of thickness. The minimum occurs at 19.0 nm
Figure 6.19: Dielectric function of a 19.0 \textit{nm} layer of AlAs.
Figure 6.20: Extracted dielectric function for a 1 Å thickness increment of a depositing GaAs layer.
be obtained by one to two orders of magnitude compared to a “chi-by-eye” approach; (2) only two (2) measurements are needed, instead of three in the exponential spiral approach; (3) the system of equations is easily inverted in contrast to the $\Delta R/R$ approach, where one has to deal with nearly singular determinants; (4) pixel-to-pixel noise does not affect the resulting values for $\epsilon_o$ and $d$ since the data is averaged over a wide range of several hundred up to almost 1000 pixels.

Note, that this approach exemplifies the necessity to remove higher order artifacts from the spectroscopic data without restricting the pixel range and without compromising time resolution.
Chapter 7

Results and Analysis

7.1 Introduction

This chapter summarizes and discusses the results obtained with the integrated RCE system, both with respect to data and to the application of methods described in previous chapters.

The purpose of the first set of experiments was to investigate the sensitivity of our instrument to optically induced anisotropy while simultaneously monitoring the pseudodielectric function. As discussed in Ch. 3, the anisotropy signal is expected to be comparable to normal incidence RDS, since the gain in sensitivity due to the proximity to Brewster’s angle for p-polarized light is lost as a result of the needed component of s-polarization.

For this set of so-called reconstruction experiments the sample ambient is manipulated to induce transitions between different reconstructions of the surface. If possible, we would like to relate the lineshapes of \( \alpha_{10} \) and \( \beta_{10} \) to RDS reference data established by Kamiya and Aspnes in both UHV and OMCVD environments [44, 45, 46, 47, 48].

In the second set of experiments the techniques discussed in Ch. 6 for extraction of the three overlayer parameters are applied to actual growth situations. In order to
achieve the ultimate goal of truly sample-driven feedback control of epitaxial growth, but also to improve the research and study of mechanisms involved in deposition processes, it is important to extract all overlayer parameters without making assumptions about the overlayer dielectric function and/or the deposition rate/thickness. Further, one can conceive of experiments where a constant growth rate simply does not exist even as an approximation. This could occur for example when a burst of material is delivered to the substrate and one would like to know how the sample responds to the given dose as a function of time.

While we have shown (Ch. 6) that wavelength-by-wavelength ($n - k - d$-) based approaches are intrinsically unstable, we can still make deliberate use of lineshape analysis to extract $\epsilon_o$ and $d$ when possible. This also fits in very well with our substantial effort made to improve the quality of the data by (1) developing a new approach for removing contributions from diffraction in second- and third-order as described in Sec. 5.5, (2) by employing the full 1024 pixel resolution, which required massive data storage capabilities and enhanced computing power, and (3) by improving the signal-to-noise ratio with a high-precision sample stage (spindle), and with high-precision, in-house built components of the rotating compensator system, in particular the rotational stage and the drive of the continuously rotating compensator.

### 7.2 Simultaneous measurement of ellipsometry and anisotropy spectra

The fundamental concept and the diagnostic advantages of our system are demonstrated in Figs. 7.1 and 7.2. First, Fig. 7.1 shows the evolution of $\alpha_{10}$ with time for an experiment in which a GaAs(001) substrate is dosed with a 1 s pulse of TMGa.
The sample was initially stabilized under 100 sccm Arsine (AsH$_3$) at a temperature of $T = 580^\circ C$. Arsine is switched out of the chamber at $t \approx 5 \text{s}$, which leads to depletion of Arsine in the chamber. A 1 s pulse of TMGa is administered at $t = 24 \text{s}$ to promote the Ga terminated $4 \times 2$ reconstruction of GaAs(001) [49, 50]. The large peak in the long wavelength range, which is centered about $t = 35 \text{s}$, is the strongest indication of the response of $\alpha_{10}$ to the Ga-pulse.

Shown in Fig. 7.2 is the imaginary part of the simultaneously measured pseudodielectric function with the time interval reduced and centered about the arrival of the Ga-pulse. Apparently, the change in the anisotropy data is accompanied by a change in the pseudodielectric function, and the depression of the $E_2$ peak at 280 nm is an indication that material is being deposited during the Ga burst.

For analysis of this experiment, the information from the pseudo dielectric function is combined with the anisotropy data as described in the following.

**Extraction of overlayer information**

First the thickness and the dielectric function of the deposited material are obtained by spectral lineshape analysis. Taking the trajectory of the $E_2$ peak of Fig. 7.3 as a guide, we can see exactly when TMGa starts to react with the surface ($t = 25 \text{s}$), when the maximum coverage with excess Ga is obtained ($t = 33.5 \text{s}$), and after AsH$_3$ is switched back into the chamber ($t = 37.5 \text{s}$), when the surface is recovered.

Taking the pseudodielectric function at $t = 25 \text{s}$ as the baseline, the maximum layer thickness is 5.75 Å. The dielectric function for this overlayer was obtained by lineshape analysis, which is possible in this case because the $E_1$- and $E_2$-peak structures from the underlying substrate coincide with the region of weak absorption of the overlayer. The extracted dielectric function shown in Fig. 7.4 It has the
Figure 7.1: $\alpha_{10}$ during Ga-dosing of GaAs(001)
Figure 7.2: $\langle \epsilon \rangle$ during Ga-dosing of GaAs (001).
Figure 7.3: The $E_2$-peak (4.42 eV) is especially sensitive to the addition or removal of overlayer material. Its trajectory reveals the timing of the TMGa pulse as seen by the sample.
characteristics of a metal with a $1/0$-singularity for $\lambda \to \infty$.

### 7.2.1 Analysis of anisotropy spectra

We still need to explain the observed lineshapes, either by direct identification (3), or by combining the knowledge of $\epsilon_o$ and $d$ from the previous section with the anisotropy data. This will allow us to understand, at least qualitatively, the spectral dependence of the signal.

The initial reconstruction under $AsH_3$ flow is shown in Fig. 7.5. This lineshape is
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<th>thickness (Å)</th>
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</tr>
</tbody>
</table>

Table 7.1: Layer thickness as a function of time during the Ga-pulse experiment as described in the text.

relatively easy to identify. It corresponds to the c/d(4x4) reconstruction, which is the predominant reconstruction in OMCVD environments [50].

The surface structure changes as AsH₃ is depleted from the reactor environment. Figure 7.6 shows the initial spectrum of α₁₀ as in Fig. 7.5 and the spectrum after 25 s of AsH₃ depletion, just before we dose the sample with TMGa. We interpret the spectrum as a residual c/d(4x4) reconstruction, which is most likely degraded due to the depletion of Arsenic from the surface. Interestingly, the predominant change at 2.4 eV coincides with the dimer energy for GaAs(001) surfaces. However, the spectrum otherwise does not correspond to a Ga-terminated 4x2 reconstruction. This is an interesting result, which could be made the subject of a further investigation.

Figure 7.7 shows the α₁₀ spectrum at t = 33.5 s, which corresponds to the maximum layer thickness. In addition to the earlier encountered changes at 2.4 eV, we see a strong structural change at the lowest energies, near 1.6 eV, which gradually
Figure 7.5: $c/d(4x4)$ reconstruction typical for OMCVD environments measured at $\theta = 70^\circ$. 
Figure 7.6: The residual c/d(4x4) reconstruction 25 s (red) after AsH$_3$ was switched into the by pass line. It appears as if the changes at 2.4 eV are related to a change in the orientation of the surface dimers, as expected when switching from an As terminated- to a Ga-terminated surface.
Figure 7.7: The anisotropy signal increases as excess Ga is deposited on the surface. This implies that the induced anisotropy is due in part to structural changes on the surface.
diminishes to zero at about 4.25\,eV. Again, this change does not coincide with any known reconstruction change of the GaAs (001) surface. However, we can use the known overlayer dielectric function from above to better describe this spectrum.

**Determination of the void fraction using the Wiener limits**

One possibility to understand the observed response is to assume that the layer itself exhibits structural anisotropy in addition to containing surface dimers. This can be modeled in a first approximation by considering an overlayer that consists of stripes of material with voids (vacuum) in between. In this fashion, we can derive the effective void fraction of the overlayer by matching the resulting values for $\Delta\epsilon$ to that needed in order to generate the observed $\alpha_{10}$ spectrum.

The dielectric function values of Fig. 7.8 together with the layer thickness obtained from ellipsometric data are used to generate $10\omega t$ coefficients for the integrated RCE. The void fraction is adjusted until the model shows the best agreement with the data.

Figure 7.9 shows the result of the calculation. Most notably is the good agreement of the overall lineshape with the data, resulting in the predominant contribution at low energies and tapering off towards higher energies. The change at the low energy end is about 0.008 in both the data and the model. However, the data show an offset, which we view as an instrument artifact at this stage.

By comparing the structural model with the data in Fig. 7.10, we can explain our reconstruction data by assuming that two factors contribute to the anisotropy signal, which are (1) the surface dimers of GaAs(001) and (2) structural anisotropy of the deposited excess Ga, which may be present in the form of elongated islands. The data in Fig. 7.10 has been offset for better comparison. However, that does not change the qualitative agreement of the underlying lineshape.
Figure 7.8: The Wiener limits for $\epsilon_o$ assuming an overlayer that consists of stripes of Ga with 1% empty space between the stripes.
Figure 7.9: From the values for $\Delta \epsilon$ resulting from Fig. 7.8 and the thickness of the anisotropic overlayer, the response of the sample is computed. Qualitatively, this simple model describes the observed lineshape for $\alpha_{10}$. 

\(\alpha_{10}, \beta_{10} - \text{model}\)
Figure 7.10: The $\alpha_{10}$ data of Fig. 7.7 (33.5 s) offset vertically to coincide with the model. This offset in the data is yet unexplained. The observed large change in $\alpha_{10}$ at the long-wavelength end can be explained, at least qualitatively, by structural changes at the surface.
In a repetition of the initial experiment, we observe that the dielectric function of the deposited film more closely resembles that of Ga compared to the first cycle. Bulk Ga reference data measured at room temperature and our extracted overlayer dielectric function, measured at 580 °C is shown in Fig. 7.11. The layer thickness 1.5 s after administration of the pulse is 3.2 Å, as obtained by lineshape analysis, and reaches a maximum of 18.5 Å. However, while the thickness after 1.5 s is comparable to the 5.75 Å of the first experiment, the overlayer dielectric function looks much more like elemental Ga.

Figure 7.11: Extracted overlayer dielectric function (3.2 Å thick) during repetition of the initial reconstruction experiment.
Table 7.2: Nominal Al-concentration as a function of the TMAI flow-rate.

<table>
<thead>
<tr>
<th>TMAI sccm</th>
<th>mol/min $\times 10^{-3}$</th>
<th>TMGa sccm</th>
<th>mol/min $\times 10^{-3}$</th>
<th>conc. x</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.247</td>
<td>5</td>
<td>4.936</td>
<td>0.20</td>
</tr>
<tr>
<td>10</td>
<td>2.49</td>
<td>5</td>
<td>4.936</td>
<td>0.34</td>
</tr>
<tr>
<td>50</td>
<td>12.47</td>
<td>5</td>
<td>4.936</td>
<td>0.72</td>
</tr>
</tbody>
</table>

7.3 $\text{Al}_x\text{Ga}_{1-x}\text{As}$, AlAs growth run - July 04, 2002

In this section we focus on the extraction of overlayer information, i.e., $\epsilon_o$ and $d$, from data obtained during growth on 04 Jul '02. Figure 7.12 gives an overview of the result, which consisted of a layer of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown on GaAs with two different concentrations $x$, followed by a layer of AlAs.

Deposition started on a GaAs(001) substrate with the growth of a GaAs buffer layer (not shown), followed by a mixed flow of TMGa and TMAI at a rate of 5 and 10 sccm, respectively. The data in Fig. 7.12 are the imaginary part of the pseudodielectric function as a function of wavelength in one direction and of overlayer thickness and composition in the other direction. The acquisition rate was 4 Hz, and ten spectra were averaged to achieve a time resolution of 2.5 s/spec.

This particular set of data is interesting because it contains two distinct transitions, the first from GaAs to AlGaAs at $t = 295$ s and the second from AlGaAs to AlAs at $t = 630$ s. Figure 7.13 shows the transient of the $E_2$ peak at 4.56 eV, which is used for timing the various transitions. Initially a alkyl precursor mixture of 5 sccm TMGa and 10 sccm TMAI is flowing into the reactor. This amounts to a theoretical alloy composition as indicated in on the graph and listed in Table 7.3.

The objective is to look for parts of the data where the underlying substrate
Figure 7.12: The imaginary part of the pseudodielectric function during growth of Al$_x$Ga$_{1-x}$As and AlAs on GaAs.
Figure 7.13: The transient of $E_2$ at 4.56 eV. Indicated are the four different stages of growth with corresponding Al-concentrations as indicated. The two main onsets are at $T = 300\, s$ and $T = 640\, s$. 
exhibits sufficient structure in the transparent region of the overlayer in order to
generate distinguishing features that are reminiscent of the substrate when overlayer
thicknesses are chosen either too small or too large. The term substrate is used
relatively freely in this context and in this case refers to a pseudosubstrate instead of
the actual substrate.

7.4 Extracting overlayer information by quantita-
tive lineshape analysis

I put the automated lineshape approach to the test by successively applying it to
the two most recently obtained spectra. The analysis is currently being performed
post-growth and cannot yet be applied in real time since with our present equipment
it takes about 75 s to analyze on set of spectra for 10 thickness increments and, on
average, 450 data points. We use a 1.7 GHz personal computer (Dell Dimension 8100)
and OriginC to perform the data analysis. However, there is also no doubt that the
computations can be made fast enough so that the algorithm can be applied in real
time.

As discussed in Sec.6.4, it is necessary that the substrate be sufficiently distinct
from the overlayer in the region where the overlayer is transparent, and that a low-
order polynomial, here a parabola, will adequately represent the true overlayer dielec-
tric function in parts of its transparent region. The latter condition is almost always
satisfied. Difficulties and restrictions must be anticipated from the first condition, i.e.,
that there is not enough structural difference between the substrate and the overlayer
material.

Of particular interest are the transition regions between two alloy compositions,
in order to see if our analysis procedure is sensitive to a change in $x$ and which is essential for integrated closed-loop feedback control. Since the substrate and the overlayer are very similar in the transparent region, and we need to grow a sufficiently thick contrast layer. After one interference oscillation has developed the transparent region, one is essentially in very good position to determine the overlayer material.

I am starting the analysis at file index 252, which corresponds to $t = 630\, s$ as the baseline and use the file with index 253 as the spectrum that contains the overlayer information. After 263 has been analyzed for its overlayer content, it becomes the next substrate, and so on.

Figure 7.16 shows the imaginary part of the extracted overlayer dielectric functions for a sequence starting four data points before the 640\, s marker at 630\, s in Fig. 7.14. The motivation to pick this particular sequence was that it coincides with a change in the alloy composition $x$ and, therefore, it is possible not only to establish the dielectric function of the outermost layer, but also to determine whether the approach is sensitive and consistent with changes in the alloy composition. Unfortunately, we do not have more transition regions available that would lend themselves to this type of analysis. However, in the case presented here, there is a nominal change in $x$ from 0.72 to 1 within the first couple of data points. The data of Fig. 7.16 shows that, not only is this lineshape procedure capable of extracting the overlayer dielectric function, but also that it is able to handle variations that along with overlayer variations and thickness.

As an example for the data we analyze here, Fig. ?? shows the merit function $\chi^2$ for 10 values of $d$ from 9 to 14.5 $\text{Å}$ for the layer deposited between $t = 635\, s$ and $637.5\, s$. The minimum of $\chi^2$ yields the best choice for the layer thickness, in this case
Figure 7.14: The trajectory of $< \epsilon >$ in the complex plane at 3.98 eV. The starting point for the lineshape approach is taken four data points to the left of the 640 s marker.
Figure 7.15: Extracted overlayer dielectric functions for time increments of 2.5 s, starting at $t = 630 \text{s}$ (index 252).
Figure 7.16: Thickness increment at $t = 635\, s$ (index 254) as determined by lineshape analysis. The minimum in $\chi^2$ yields the best choice for $d$.

9.5 Å. The uncertainty due to statistical noise is $7.34 \times 10^{-3}\, \text{Å}$, however, that only accounts for pixel-to-pixel noise but not spectrum-to-spectrum fluctuations, which may be significantly higher. Again, this demonstrates that the method of representing the spectral dependence of $\epsilon_o$ by an analytic expression eliminates the noise problem, which is encountered when derivatives are taken with respect to wavelength [43].

The trajectory of the $< \epsilon >$ in the complex plane is given in Fig. 7.14. It helps to interpret the data by means of identifying the different alloy compositions.

Table 7.4 lists the thicknesses obtained from lineshape analysis. It is not surprising
that the growth rate increases as indicated, since the flux of TMAI is increased from 10 to 5 sccm, which leads to an abrupt increase in $x$ from 0.34 to 0.72.

The $E_1$ transition in the sequence of Fig. 7.16 increases with time as it should with increasing aluminum concentration. The imaginary part of the overlayer dielectric function goes to zero for long wavelengths as it has to. This condition is sometimes used to reduce the number of unknowns to two instead of three [51]. However, here we use it as a self-consistency check on the obtained data, since no assumptions about the overlayer are made. Finally, the relatively broad $E_1$ transitions are also consistent with the deposition of thin films.

<table>
<thead>
<tr>
<th>index</th>
<th>time (s)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>252</td>
<td>630</td>
<td>6.7</td>
</tr>
<tr>
<td>253</td>
<td>632.5</td>
<td>6</td>
</tr>
<tr>
<td>254</td>
<td>635</td>
<td>9.5</td>
</tr>
<tr>
<td>255</td>
<td>637.5</td>
<td>33.9</td>
</tr>
<tr>
<td>256</td>
<td>640</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Table 7.3: Obtained thickness increments between spectra as discussed in text.
Chapter 8

Conclusion

We have built a state-of-the-art, integrated rotating-compensator ellipsometer/polarimeter for real-time diagnostics of OMCVD processes, and used it to obtain information about AlGaAs growth in real time. What makes our configuration special are: (1) integration with a commercial turbo disk reactor, where we synchronize compensator and sample rotation, which allows us to simultaneously obtain both the optically induced anisotropy and the ellipsometry signals and which also reduces apparent noise; (2) a spindle that allows sample runout to be adjusted during rotation, eliminating beam-wobble artifacts; and (3) and (4) a high performance optical spectrometer and data-processing and storage in real time, which allows us to acquire spectra of 1024 wavelengths from 240 to 840 nm at a rate of 5 Hz.

Since our detector measures absolute intensities, the entire, accessible information content of the light beam is made available through $|r_p|^2$, $|r_s|^2$, and $\tilde{r}_p \tilde{r}_s^*$, which are returned by the RCE. A fourth quantity, the overall (or absolute) phase, cannot be determined with present technology. $|r_p|^2$ and $|r_s|^2$ yield the magnitudes for p- and s-polarized waves, and $\tilde{r}_p \tilde{r}_s^*$ yields the relative phase $\Delta$. Thus all the information contained in the beam with the exception of absolute phase is available for analysis.
We formulate the data-analysis problem in these parameters rather than the complex reflectance ratio commonly used.

Special care was taken during the design of the instrument to ensure reliable, low-noise operation of all of its components, in particular of the rotational stage that receives the $MgF_2$ waveplate and the spindle, which supports and orients the sample.

The data-acquisition routines were tailored for high performance real-time operation. A multi-threaded C++ data-acquisition program has been developed, which features compact acquisition routines to operate in real-time mode. Thereby, almost the entire CPU time is devoted to execution of these routines in order to minimize the response time of the computing module. Upon exit of the data acquisition routine, the corresponding thread becomes dormant and requires only minimal process time while waiting for the next set of data. In this way, the system response time is minimized while other necessary routines are still being executed in between the real time threads. Obviously, this prevents the system from locking-up and it frees necessary resources for the execution of further routines, for instance, to update the display and to write the data to the hard disk.

A previous detector dead time of 50% due to a time-consuming call to an external fast Fourier routine has been eliminated by placing the Fourier transform directly into the data-analysis routine. The rate-limiting steps are now the readout time of the photo diode array and the speed by which data can be written to the hard disk. The maximum acquisition rate is close to $6\ Hz$, with the upper limit being set by the minimal readout time of the camera. When the data also need to be stored, the maximum acquisition rate is slightly less, about $5 - 5.5\ Hz$.

The rotating compensator ellipsometer is considerably harder to calibrate than
the rotating polarizer system it replaced, as described in Ch. 5. We developed entirely new calibration routines which take advantage of the spectral capability of the instrument, for instance for calibrating the polarizer and to minimize the effect of optical activity on the analyzer calibration.

Treatment of higher-order diffraction artifacts in the broadband camera posed a special problem. More than 60% of the spectral information is distorted due to overlapping intensities from second- and third-order diffraction. Therefore, it was essential to remove these artifacts since no serious measurement is possible in their presence. My solution is the numerical procedure described in Sec. 5.5, where a self-consistently determined correction is applied to the intensity read-out at each diode. No similar approaches were found anywhere in the literature, so I assume that the present approach is unique.

Having $|r_p|^2$, $|r_s|^2$ and $\tilde{r}_p \tilde{r}_s^*$ available for analysis, an obvious next step was to investigate whether these data could be combined to solve the n-k-d problem on a wavelength-by-wavelength basis to uniquely determine the properties of the overlayer parameters in the three-phase model.

The numerical results of Ch. 6 show that this problem is essentially not solvable for data obtained with present and foreseeable instruments. This result is interesting also because technically a solution exists as shown in Appendix C, where I prove that the determinant must vanish for analytic functions. Accordingly, since $|r_p|^2$ and $|r_s|^2$ are non-analytic, the existence of the solution is generally guaranteed.

The numerical difficulties can be related to the functional similarity between $\tilde{r}_p$ and $\tilde{r}_s$ when expressed in the three-phase model, as well as the weak sensitivity of s-polarized light to the presence of an overlayer. The numerical/quantitative analysis
of the Jacobian matrix, which determines the characteristics of the resulting system of equations, shows that the numerical degree of independence is vanishingly small and explains the observed amplification of small data errors with the strong tendency of the solution to become unstable and to diverge.

Accordingly, I have developed a second approach based on the well-understood concept of residual lineshape analysis with a new variation, which is my initial step for quantification of this method. The basic idea is to note that spectral features of the substrate, including interference oscillations, cannot appear in the determined dielectric function of the overlayer if these are different materials. In contrast to earlier work by Arwin and Aspnes [43], analysis is done quantitatively instead of qualitatively, no derivatives are taken of the data, and no assumptions about the physical origin of the observed lineshape are made. Instead, I fit low-order polynomials to the extracted overlayer dielectric function and adjust the thickness until the residual $\chi^2$ takes on its minimum, which corresponds to the actual layer thickness. This method is effective because it is virtually independent of pixel-to-pixel noise and because it requires no serious assumptions to be made about the overlayer other than identifying the best spectral range for fitting.

Finally, I combine these advances by applying them to the growth of AlGaAs on GaAs as described in Ch. 7.3. In particular, I extract extract overlayer dielectric functions and layer thicknesses without making any assumptions about the growth rate or the material that is being deposited. My approach thus goes far beyond current practices, where some type of assumption is typically made to effectively reduce the number of unknowns to two.
I use the lineshape-analysis method to determine the thickness and overlayer dielectric function of films as thin as one (1) Ångstrom. This is clearly a very promising candidate for extracting all three overlayer parameters from optical data in real time. The remaining computational challenges to achieving real-time analysis are relatively small in comparison and are essentially centered about making the algorithm sufficiently fast. However, this should not pose a serious problem, because the necessary increase in computational power relative to our PC is only about one to two orders in magnitude and hence already available commercially.
Appendix A

Intensity Calculation for the Polarizer-Sample-Analyzer Configuration

The intensity calculation for the polarizer-sample-analyzer configuration is carried out in Jones’ matrix notation. As usual, the calculation proceeds by (1) identifying the component matrices, (2) calculating the resulting system matrix, (3) determining the transmitted electric field vector, and (4) calculating the absolute squared of the transmitted field.

1. The matrix representations for polarizer and analyzer are

\[
\begin{align*}
\tilde{P}(P) &= \begin{pmatrix}
\cos P - i\gamma_p \sin P & i\gamma_p \cos P \\
-\sin P - i\gamma_p \cos P & -i\gamma_p \sin P
\end{pmatrix} \\
\tilde{A}(P) &= \begin{pmatrix}
\cos A + i\gamma_a \sin A & -\sin A + i\gamma_a \cos A \\
-i\gamma_a \cos A & i\gamma_a \sin A
\end{pmatrix}
\end{align*}
\] (A.1) (A.2)

, respectively. The sample is the standard diagonal matrix

\[
\tilde{R} = \begin{pmatrix}
\tilde{r}_p & 0 \\
0 & \tilde{r}_s
\end{pmatrix}.
\] (A.3)
2. The components need to multiplied from left to right to obtain the system matrix

\[ \tilde{S} = \tilde{A}(A)\tilde{R}\tilde{P}(P) \]  

(A.4)

3. The incident electric field is a 2d vector and has the form

\[ \vec{E}_i = E \begin{pmatrix} 1 \\ 0 \end{pmatrix} \]  

(A.5)

and the transmitted electric field is

\[ \vec{E}_t = \tilde{S}\vec{E}_i \]  

(A.6)

Of the four elements of the system matrix only \( S_{11} \) and \( S_{21} \) need to be considered, since the \( y \)-component of the representation of the incident electric field vector is zero.

\[ S_{11} = \tilde{r}_p (\cos P - i\gamma_p \sin P) (\cos A + i\gamma_a \sin A) \]
\[ - \tilde{r}_s (\sin P + i\gamma_p \cos P) (-\sin A + i\gamma_a \cos A) \]
\[ S_{21} = -i\gamma_a \cos A (\cos P - i\gamma_p \sin P) - i\gamma_a \sin A (\sin P + i\gamma_p \cos P) \]
\[ = O(\gamma_a). \]  

(A.7)

4. The intensity is obtained by evaluating the sum \( |S_{11}|^2 + |S_{21}|^2 \). I am going to consider the effect of optical activity only to first order, so that \( |S_{21}|^2 \) can be neglected. Evaluation of \( |S_{11}|^2 \) yields equation 5.2.1:

\begin{align*}
I \propto |S_{11}|^2 &= |\tilde{r}_p|^2 \cos^2 A \cos^2 P + |\tilde{r}_s|^2 \sin^2 A \cos^2 P \\
&+ \frac{1}{4} (\tilde{r}_p\tilde{r}_s^* + \tilde{r}_s\tilde{r}_p^*) \sin 2A \sin 2P \\
&+ \frac{i}{2} (\tilde{r}_p\tilde{r}_s^* - \tilde{r}_s\tilde{r}_p^*) (-i\gamma_p \sin 2A + i\gamma_a \cos 2P) \\
&+ O(\gamma_a^2, \gamma_p^2, \gamma_a \gamma_p) \\
\end{align*}  

(A.8)
Appendix B

Spindle Shaft
Arbor piece

Material: stainless steel
conical cutout with 30 degree cone angle

Figure B.1: The arbor piece.
Figure B.2: Stainless steel cube.

Cube

Material: stainless steel
tppered drill through:
1/4–28,
2" X 1/16" circular recess with 1/4" diam.
Rocking disc

material: stainless steel
conical bore cut with 30 degree cone angle.
30 degree v-groove

side view: 90 degree rotated

Figure B.3: Rocking disk.

Wobble stick

Material: stainless steel
threaded end: 1/4”-28

Figure B.4: Control stick.
Appendix C

Singular determinant of the Jacobian for analytic functions

Assume that \( \tilde{r}_p = \tilde{r}_p(\epsilon_{o,r}, \epsilon_{o,i}, d) \) and \( \tilde{r}_s = \tilde{r}_s(\epsilon_{o,r}, \epsilon_{o,i}, d) \) are analytic functions of \( \epsilon_o \)

\[
\begin{align*}
\tilde{r}_p &= \tilde{r}_{p,r}(\epsilon_{o,r} + i\epsilon_{o,i}) + i\tilde{r}_{p,i}(\epsilon_{o,r} + i\epsilon_{o,i}) , \\
\tilde{r}_s &= \tilde{r}_{s,r}(\epsilon_{o,r} + i\epsilon_{o,i}) + i\tilde{r}_{s,i}(\epsilon_{o,r} + i\epsilon_{o,i}) ,
\end{align*}
\]

(C.1)

so that the Cauchy relations

\[
\begin{align*}
\frac{\partial \tilde{r}_{p,r}}{\partial \epsilon_{o,r}} &= + \frac{\partial \tilde{r}_{p,i}}{\partial \epsilon_{o,i}} \\
\frac{\partial \tilde{r}_{p,r}}{\partial \epsilon_{o,i}} &= - \frac{\partial \tilde{r}_{p,i}}{\partial \epsilon_{o,r}}
\end{align*}
\]

(C.2)

are satisfied for both \( \tilde{r}_p \) and \( \tilde{r}_s \). Further, suppose we construct a vector of three functions

\[
\vec{F} = \begin{pmatrix} f_1 \\ f_2 \\ f_3 \end{pmatrix}
\]

(C.3)

where the \( f_i = f_i(\tilde{r}_p, \tilde{r}_s) \) are also analytic functions.

The Jacobian is formed from \( \vec{F} \) by taking the derivatives
\[ J_{ij} = \frac{df_{ij}}{dx_i}, \]  
\[ \text{(C.4)} \]

where \( \vec{x} = (\epsilon_{o,r}, \epsilon_{o,i}, d) \).

Developing the determinant after the first column yields

\[
\text{DET} (J) = \left( \frac{\partial f_2}{\partial r_p} \frac{\partial f_3}{\partial r_s} - \frac{\partial f_2}{\partial r_s} \frac{\partial f_3}{\partial r_p} \right) \\
\left[ \frac{df_1}{d\epsilon_{o,r}} \left( \frac{dr_p}{d\epsilon_{o,i}} \frac{dr_s}{dd} - \frac{dr_p}{dd} \frac{dr_s}{d\epsilon_{o,i}} \right)_I - \frac{df_1}{d\epsilon_{o,i}} \left( \frac{dr_p}{d\epsilon_{o,r}} \frac{dr_s}{dd} - \frac{dr_p}{dd} \frac{dr_s}{d\epsilon_{o,r}} \right)_II + \frac{df_1}{dd} \left( \frac{dr_p}{d\epsilon_{o,r}} \frac{dr_s}{d\epsilon_{o,r}} - \frac{dr_p}{d\epsilon_{o,i}} \frac{dr_s}{d\epsilon_{o,r}} \right)_III \right]. 
\[ \text{(C.5)} \]

Also,

\[
\frac{df_1}{d\epsilon_{o,r}} = \partial f_1 \frac{dr_p}{dr_p} + \partial f_1 \frac{dr_s}{d\epsilon_{o,r}}, 
\]
\[ \text{(C.6)} \]

with the corresponding expressions for the derivatives with respect to \( \epsilon_{o,i} \). Using Cauchy’s relations it follows that \((\ldots)_{III}\) is identically zero, so that we are left with the first two brackets \((\ldots)_I\) and \((\ldots)_{II}\). Expanding the derivatives of \( f_1 \) according to Eq. (C.6) gives

\[
[\ldots] = \frac{\partial f_1}{\partial r_p} \left[ \frac{dr_p}{d\epsilon_{o,r}} (\ldots)_I - \frac{dr_p}{d\epsilon_{o,i}} (\ldots)_{II} \right] + \frac{\partial f_1}{\partial r_s} \left[ \frac{dr_s}{d\epsilon_{o,r}} (\ldots)_I - \frac{dr_s}{d\epsilon_{o,i}} (\ldots)_{II} \right], 
\]
\[ \text{(C.7)} \]

but \( \frac{dr_p}{d\epsilon_{o,i}} = i \frac{dr_p}{d\epsilon_{o,r}} \), so that

\[
\text{DET} \left( \bar{J} \right) = \left( \frac{\partial f_2}{\partial r_p} \frac{\partial f_3}{\partial r_s} - \frac{\partial f_2}{\partial r_s} \frac{\partial f_3}{\partial r_p} \right) \left[ \frac{\partial f_1}{\partial r_p} \frac{dr_p}{d\epsilon_{o,r}} + \frac{\partial f_1}{\partial r_s} \frac{dr_s}{d\epsilon_{o,r}} \right] [\ldots]_I - i [\ldots]_{II}. 
\]
\[ \text{(C.8)} \]

It is straightforward to show that the term in square brackets on the right is identically zero:
\((\ldots)_I - i (\ldots)_II = -\frac{dr_p}{dd} \left( \frac{dr_s}{d\epsilon_{o,i}} - i \frac{dr_s}{d\epsilon_{o,r}} \right) + \frac{dr_s}{dd} \left( \frac{dr_p}{d\epsilon_{o,i}} - i \frac{dr_p}{d\epsilon_{o,r}} \right) = 0, \quad (C.9)\)

where both brackets on the right vanish identically when Cauchy’s relations are applied. \textit{q.e.d.}
Bibliography


