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Ellipsometry of Functional Organic Surfaces and Films

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Foreword

Given the continuing and increasing role of spectroscopic ellipsometry (SE) as a real-time non-destructive monitoring/characterization tool in numerous technological and biomedical applications, the editors, authors, and Springer are commended for publishing this monograph which is dedicated to significant applications of SE to functional organic surfaces and thin films. Topics include the adsorption of biomolecules at liquid-solid interfaces, smart polymer surfaces and thin films for sensor applications, characterization of nanoparticles and nanostructured surfaces and thin films, and thin-film organic semiconductors for photovoltaics and light emitters. The book also covers recent developments of SE instrumentation and related techniques over a broad optical bandwidth.

This monograph is a welcome addition to the ellipsometry literature.

University of New Orleans R.M.A. Azzam

Preface

For more than a century, ellipsometry has been utilized by physicists as a non-destructive, absolute and thin film sensitive optical method to determine index of refraction and absorption of solid materials (metals, semiconductors, oxides). Over the last few decades, user-friendly ready-to-use ellipsometers have been developed spanning the far-infrared to ultraviolet spectral range. Continuing advances in experimental ellipsometric techniques and theory have enabled researchers to tackle challenges in modern material science such as research of superconductors and metamaterials, rough and nanostructured surfaces, complex hybrid films as well as spintronics, plasmonics and magnetooptics [1, 2, 3]. Nevertheless, if one were to ask a chemist or biologist working with organic surfaces and thin films "What is ellipsometry?" the answer will often be: "It is a nice method to quickly and easily measure film thickness". However, although the technique is considered highly accurate, it is often viewed as somewhat exotic and difficult to understand.

This book intends to bridge this gap and aims to overcome certain prejudices ("ellipsometry is a black box..."). It presents ellipsometry to scientists as a versatile method for chemical, biological and material science applications dealing with small and large organic molecules on surfaces. Prime examples are the study of synthetic polymers with different architectures and functionalities, as well as biopolymers. The analysis of functional surfaces often requires new methods to apply ellipsometry for quantitative, non-destructive, label-free and contact-less characterization. Most of the authors of this book, as well as we the editors, have been active in the application and development of ellipsometry for many years and were interested in applying ellipsometry to studies of functional organic films. The close cooperation in an interdisciplinary field between chemistry, physics, material sciences and biotechnology was necessary to tackle such analysis. Nevertheless, it is important to mention that there is a broad still developing field of analysis and ellipsometric methods for better understanding of complex and structured samples and materials. In particular promising attempts have been made in combination with Rigid Coupled Wave Analysis and Finite element calculations in the study of complex samples. Fundamentally such methods and theory might also be helpful for better understanding of dipole or wave interactions as well as the analysis of material variations in the nanometer scale. Recently developed scanning infrared near field ellipsometry might be another puzzle piece for working on this topic.

Of course, a zoo of modern microscopic, spectroscopic and also physical-chemical methods are known and widely applied for the characterization of organic surfaces and thin films. They play an important role in the "daily life" of the material scientist, for example XPS, SIMS, AFM, SEM, X-ray and neutron reflection, photoluminescence, fluorescence, FTIR- and Raman spectroscopy, mass spectrometry, inverse GC, contact angle and Zetapotential measurements and many more. Cooperatively applied ellipsometry can determine thicknesses and complementing anisotropic optical and structural properties in a non-contact and non-destructive manner in various environments. The different chapters of this book demonstrate the possibilities, advantages and problems of application of (mainly spectroscopic) ellipsometry. In comparison to many other methods ellipsometry as an optical technique is relatively easy to do under normal lab conditions. Using special cells, temperature-dependent in situ experiments in vacuum, gaseous and liquid ambient are possible. A sometimes more challenging task is the evaluation of the experimental (optical) data to obtain the desired physical and chemical information on the films and surfaces.

In the following chapters, worldwide recognized experts from universities and research institutes give examples and actual results in studies applying ellipsometry to different aspects of functional organic surfaces and thin films:

As theoretical introduction C. Cobet gives an overview about the ellipsometric method, including history, basics and principles, experimental techniques and optical models for data evaluation.

The experimental examples begin with "Biomolecules at surfaces". H. Arwin shows why ellipsometry is an excellent tool to study many aspects of protein adsorption at solid surfaces. DNA structures on silicon and diamond are the focus of the special chapter by S.D. Pop and colleagues.

"Smart polymer surfaces and films" are actual materials of interest for applications as organic sensors, actuators or bioactive/bioinert surfaces. The glass transition in thin polymer films remains a controversial topic, however M. Erber et al. demonstrate that it may be studied very comfortably by spectroscopic ellipsometry (SE). In situ ellipsometry is necessary to study polymer brushes, hydrogels and polyelectrolyte multilayers—typical stimuli-responsive systems. E. Bittrich et al. give an overview of recent results of smart polymers and the protein adsorption at these soft organic surfaces.

In the first chapter of Part "Nanostructured surfaces and organic/inorganic hybrids" T. Oates demonstrates how systems consisting of nanoparticles and polymers or self-assembled monolayers can be characterized by appropriate ellipsometric methods. In the next chapter, complicated nanostructured (sculptured) thin films with high anisotropy are presented by K.B. Rodenhausen et al. These highly ordered 3-dimensional structures and, moreover, organic attachment onto such surfaces, may be characterized by advanced ellipsometric techniques. Similar techniques are necessary to describe polarizing natural nanostructures (e.g. surfaces of beetles) as is shown in the last chapter of this part by K. Järrendahl and H. Arwin.

"Thin films of organic semiconductors" play an outstanding role in organic electronics and the development of OPV, OLED and OTFT. Optical properties from UV to IR range, morphology and molecular orientation may be excellently characterized by spectroscopic ellipsometry. Large molecules as important polymers, blends and composites are the focus of the report of S. Logothetidis from Thessaloniki, whereas O. Gordan and D.R.T. Zahn describe ellipsometric measurements on films of small organic molecules.

"Developments in ellipsometric real-time/in-situ monitoring techniques" are presented in Part V. A main point here is, again, the solid-liquid interface. It is possible to study the behavior of organic surfaces and thin films in their natural and also (artificial) liquid environment. R.P. Richter et al. show the power of coupled complementary methods, namely QCM-D with spectroscopic ellipsometry (SE). Total Internal Reflection Ellipsometry (TIRE) and SPR-enhanced SE are introduced by H. Arwin as emerging techniques with very high sensitivity and precision for studying adsorption processes. The combination of SE in the mid-infrared spectral range and electrochemistry provide fascinating insights into the chemistry of thin organic films as described by J. Rappich et al. And last but not least, it is possible to use SE for the in-line quality control of organic thin film fabrication on rigid and flexible substrates. In their chapter of Part V A. Laskarakis and S. Logothetidis give an overview on the state-of-the-art in this field.

Infrared ellipsometry (IRSE), but also other surface-sensitive FTIR spectroscopic methods for the characterization of thin organic films are reviewed by K. Roodenko et al. in Chap. 15. Their focus is on the evaluation of molecular structure and orientation.

Using the brilliant infrared light from a synchrotron source makes it possible to perform far field micro-ellipsometric studies with good lateral resolution. In Chap. 16, M. Gensch presents the technical background and interesting applications and outlook.

It is of great interest to anyone who would like to use spectroscopic ellipsometry to study thin organic film of polymers or small molecules to have an idea on their optical constants (refractive index and extinction coefficient). Thus, the last Part of the book provides support in this direction: A. Furchner and D. Aulich present a collection of optical constants of organic thin film materials. Such optical constants are an excellent starting point in the interpretation and optical modeling of spectra of related materials, however they may vary in details for the specific case.

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Berlin, Germany — Karsten Hinrichs
Dresden, Germany — Klaus-Jochen Eichhorn

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Chapter 1
Ellipsometry: A Survey of Concept

Christoph Cobet

Abstract Already the first attempts by Paul Drude in the late 19th century demonstrate the abilities of optical polarimetric methods to determine dielectric properties of thin layers. Meanwhile ellipsometry is a well-established method for thin film analysis. It provides material parameters like n and k even for arbitrary anisotropic layers, film thicknesses in the range down to a few Ångström, and ellipsometry is used to analyze the shape of nm-scale surface structures. But, the determination of such manifold information by means of light polarization changing upon reflection at a sample surface requires appropriate optical models. This introductory chapter will provide a general overview and explanation of theoretical and experimental concepts and their limitations. It will introduce the very basic data evaluation steps in a comprehensive manner and will highlight the principal requirements for the characterization of functional organic surfaces and films.

1.1 Classification

Ellipsometry and other types of polarimetry are well known optical methods which are used since more then 100 years for analytic purposes. Here, the term ellipsometry is certainly linked to the polarization sensitive optical investigation of planar solid state structures (metals, semiconductors) with polarized light. Optical methods in general benefit from the fact that they are usually non destructive and applicable in various environments. The object under investigation can be stored in vacuum, gas, liquid, and even in solid ambiances as long as the surrounding material is transparent within the spectral range of interest. By taking advantage of the polarizability of light, it is possible to measure for example thin film properties like the refractive index and the thickness with very high accuracy and without the need of a reference. Because of these abilities ellipsometry is meanwhile a very popular method used in many different application fields. Accordingly, a couple of books, book chapters,

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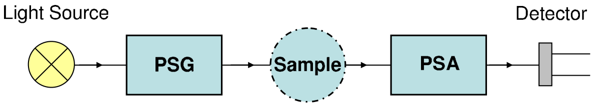

Fig. 1.1 Principle concept of ellipsometric and polarimetric techniques. The Polarization State Generator (PSG) and Polarization State Analyzer (PSA) may consist of a polarizer or a combination of a polarizer and retardation component

and review articles provide already comprehensive information about the method ellipsometry itself and the physical/mathematical background especially for thin film applications [1–7]. Therefore, it is not the intention to repeat here once again all technical details. We would rather like to provide in this chapter an overview about relevant aspects which are needed to empathize the analytical possibilities concerning functional organic surfaces and films. Furthermore, we will address limitations of the method and the underlying physical models.

The common concept behind the methods ellipsometry and polarimetry rests upon the analysis of a polarization change of light which is interacting with the object of interest. Here, we follow one of the definitions given by Azzam [8] in 1976 which was discussed in connection to the 3rd International Conference on Ellipsometry. Accordingly "An ellipsometer (polarimeter) is any instrument in which a TE-EMW—transverse electric electromagnetic wave—generated by a suitable source is polarized in a known state, interacts with a sample under investigation, and the ellipse (the state of polarization) of the radiation leaving the sample is analyzed". This concept implies that both the polarization state of the light before and after interaction with the sample can be modified or determined (Fig. 1.1). Investigations for example of atmospheric and extraterrestrial phenomena where the polarization properties of the light source itself are analyzed or where the light polarization before interacting with the object of interest is not accessible are not considered in this definition [9]. Furthermore, only linear optical effects are considered and phenomena, where the light frequency is changed like in Raman scattering, second harmonic generation and sum frequency processes, are excluded.

With the definition above, ellipsometry can be used to analyze reflected, transmitted, scattered, and diffracted light (Fig. 1.2). Ellipsometric transmission measurements are so far preferentially used to analyze birefringence, optical activity, circular birefringence, and in case of a small absorption also circular dichroism. In this book the discussion is focused on the analysis of organic surfaces and stratified films in reflection type measurements. Thus, the sample is illuminated under an oblique angle of incidence and the specular reflection is analyzed (Fig. 1.2(a)). Accordingly, all presented theoretical models assume that the analysis takes place in the optical far field where the approximation of plane waves is reasonable i.e. the distance between analyzer/detector and the sample has to be much larger than the wavelength and possible lateral inhomogeneities of the sample.

The applied optical models assume furthermore monochromatic or quasi-monochromatic electromagnetic waves which are reflected at the sample by retaining total polarization of the incident light. The electromagnetic wave before and

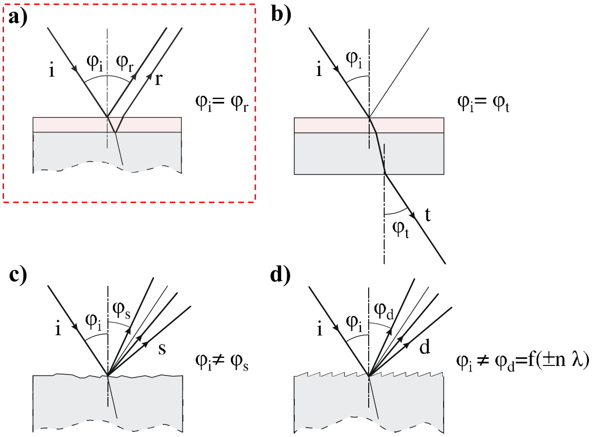

Fig. 1.2 Fundamental interaction of light which incidents on different samples under an angle φ_i: (**a**) reflection, (**b**) transmission, (**c**) scattering, and (**d**) diffraction. All introduced ellipsometric problems are reflection measurements (*red dashed box*)

after reflection is completely defined by an unique elliptical polarization state which gives the method the name "ellipsometry".

The term "polarimetry", in contrast, is usually used in a more general context including the analysis of non-specular reflected or scattered light from inhomogeneous samples or surfaces (Fig. 1.2(b–d)). In this context polarimetry is often used as a contact free method in order to determine morphology aspects [10]. Strongly related to scattering processes is a partial depolarization of the light. As we will discuss later, this requires extended optical models. A strict delimitation between ellipsometry and polarimetry, however, is neither possible nor helpful. In reality both terms are used with much overlap and a number of specific approaches are used by related proper names (Sect. 1.5.6).

Bearing in mind that the fundamental electromagnetic theory remains the same for all different regions of the spectrum, it is also not surprising that methods like polarimetry and ellipsometry are applied in much the same way from the region of radio frequencies over the infrared, visible and ultra violet to the X-/γ-ray spectral range. But due to experimental peculiarities, the knowledge transfer between the communities is unfortunately low. This book will bridge in parts this spacings by including all sections of the "optical" spectral range which includes here the infrared, the visible, and the ultraviolet wavelength/frequency range. Nevertheless, it could be particularly beneficial to consider also applications in the radio, radar, and microwave region. Related to the longer wavelength, the determination of structural and morphological properties in this range is historically stronger in the focus. Respective theoretical models for the data processing are therefore rather sophisticated and can be adapted for the optical spectral range [9, 11].

1.2 Historical Context

In a historical review the first observations of the polarization properties of light is directly linked to the discovery that light changes its polarization state after reflection on, for example, glass windows of buildings and is associated with names like Etienne-Louis Malus, David Brewster, and Augustin-Jean Fresnel. In the 1800's the polarization change of reflected light was used in a couple of works to study the optical properties of metals. A first description of elliptically polarized light attributes to Jamin [12–14]. He has observed this polarization after reflection of linearly polarized light on metal surfaces which were decorated with transparent overlayers. It turned out, that the elliptical polarization is the most arbitrary polarization state whose constituting parameters have to be determined when planar homogeneous layers are investigated.[1] For this reason, the name "ellipsometry" was established by Rothen [15] almost 100 years later in 1945 for such kind of measurements. However, a first comprehensive description of the method as a technique to study the optical properties of thin films was given already by Paul Drude in the late 19th century. He was measuring the optical properties of metals under consideration of unintentional and intentional overlayers. Furthermore, he could model the measured polarization changes by an extension/modification of Fresnel's equation, which are originally made for the reflection of light on a single planar interfaces, to the problem of two stacked interfaces [16–18]. With this approach it was possible to determine bulk and film dielectric properties as well as film thicknesses.

70 years later these analytical potentials attract a lot of attention in connection with the invention and development of semiconductor electronics. The investigation of SiO_2 films on Si is probably one of the best examples for the abilities of the method until now. On the other hand, the progress in semiconductor electronics considerably accelerates the development of computers and the automation possibilities. With the help of microprocessors it was now possible to build automatic spectroscopic ellipsometers (SE) which made the method much more attractive for a wider community. Large steps forward in development and improvement are associated to the work of Aspnes [19]. This progress also lead to more advanced applications and setups with an appropriate spectral range and a reasonable resolution. In the following different angles of incidence or different polarization states of the incident light were used in order to extract more accurate information from rather complex samples. Meanwhile multi-layer structures, all kinds of optical anisotropy, magneto-optical effects, as well as 3D inhomogeneous structures are accessible. But the final breakthrough for the method is definitely linked to the availability of easy-to-use analysis software packages. Hence, it became possible to extract useful information even for complicated sample structures with moderate efforts. In this context it is also apparent why the optical characterization of organic films, which are often anisotropic and inhomogeneous, was mostly restricted to reflection and transmission measurements for a long time. The wide spread developments in the recent years are documented for example in the proceedings of the conference series "International Conferences on Spectroscopic Ellipsometry" [20–24]. Concerning the newer developments we would also refer to a number of publications which provide further details [8, 25–29].

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[1] Possible contributions of unpolarized light are ignored here.

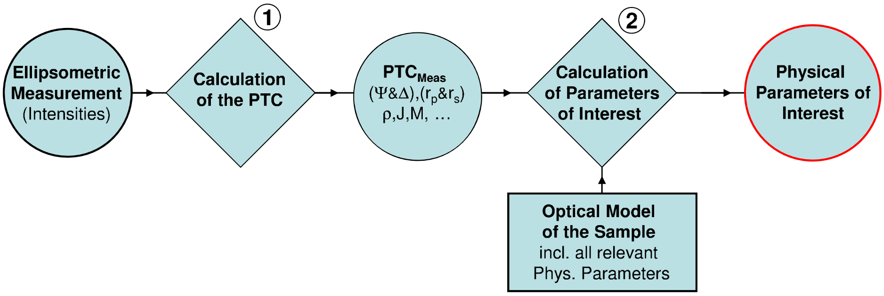

Fig. 1.3 Basic data evaluation steps in an ellipsometric measurement. The *left hand side* of the flow chart depicts the determination of the polarizing properties of the sample which are represented e.g. by the ellipsometric angles Ψ and Δ or in more general by polarization transformation coefficients (PTC). In the *right hand part* these polarization parameters are translated in physical sample parameters with the help of a qualitative sample model

1.3 Measurement Principles

1.3.1 Data Recording and Evaluation Steps

As it was mentioned, ellipsometry in principal determines polarization changes upon interaction with a sample. Subsequently it is possible to extract, for instance, layer thicknesses or dielectric properties in a "reference free" manner. Thus, two major data evaluation steps are needed in ellipsometry in order to receive information about the sample (Fig. 1.3). In parts they depend on each other. Nevertheless it is helpful to divide the problem in such basic steps and it seems worthwhile to discuss these steps briefly to obtain a general understanding of the method.

All kinds of ellipsometers are primary measuring intensities with light sensitive detectors. These intensities have to be related in the first evaluation step to the polarization change induced by the sample (left hand part of Fig. 1.1). Therefore, each ellipsometer is recording the intensity with different incident light polarizations or analyzer orientations in order to obtain relative intensities. With an appropriate set of such arrangements one can deduce out of it, how the sample under investigation changes an arbitrary polarization of the incident light. It is evident that a respective theoretical formalism is needed which translates the detector signals to the polarization properties of the sample. As it will be discussed later, the probability of the sample to change the polarization of monochromatic light can be described for an isotropic sample, if no depolarization takes place, by two parameters. Quite often the so-called ellipsometric angles Ψ and Δ are used. In case of anisotropic structures up to 6 parameters are needed. According to reference [8] these parameters are denoted here as "polarization transformation coefficients" (PTC). If depolarization effects are apparent, the number of parameters increases even further. For the moment it is important to note that the PTC's depend on the angle of incidence, the wavelength, and probably on the sample orientation, too.

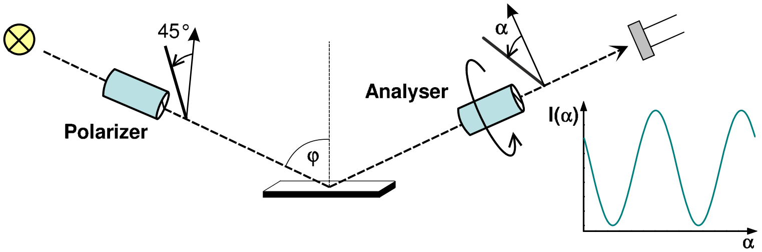

Fig. 1.4 Principal of a rotating analyzer ellipsometer. The polarizer is here fixed with the transmission axis tilted by 45° with respect to the plane of incidence. The intensity signal recorded at the detector for a certain wavelength by rotating the analyzer is of a sinusoidal form with a periodicity of 2α

A very common and simple ellipsometer is the so-called rotating analyzer ellipsometer. It's principle arrangement and the signal recorded at the detector by rotating the analyzer is shown in Fig. 1.4 (q.v. Sect. 1.5). With at least three different analyzer positions it is possible to assign the sinusoidal dependence of the intensity as a function of the rotation angle α by means of the two $\sin(2\alpha)$ and $\cos(2\alpha)$ Fourier-coefficients s_2 and c_2, respectively. With the later briefly explained mathematical formalism it is possible to calculate Ψ and Δ of an isotropic non-depolarizing sample according to

$$\tan\Psi = \sqrt{\frac{1+c_2}{1-c_2}}, \qquad \cos\Delta = \frac{s_2}{\sqrt{1-c_2^2}}. \tag{1.1}$$

In a second step the information about the polarization change by the sample (the PTC's or Ψ and Δ) should be translated in to intrinsic sample properties which are not anymore related to a certain measurement configuration (right hand part in Fig. 1.3). Such intrinsic sample properties are, for instance, layer dielectric functions, layer thicknesses, or volume fractions in inhomogeneous media.

In order to calculate intrinsic properties from the PTC's again, an adequate theoretical description is required. This means that the reflection process depicted in Fig. 1.2(a) has to be specified in more detail. In the very simple and ideal case of a planar abrupt surface of a infinitely thick isotropic sample this connection is given by the well known Fresnel equation. The hereby defined reflection coefficients r_p and r_s for light polarizations parallel and perpendicular to the plane of incidence determine the ellipsometric angles Ψ and Δ:

$$\frac{r_p}{r_s} = \tan\Psi e^{i\Delta}. \tag{1.2}$$

Light reflection from the backside of the sample is neglected in this model. For stratified anisotropic media optical layer models are used in order to calculate the respective PTC's for a given sample structure. In many cases, it is nevertheless possible to define generalized Fresnel equations. The sample parameters are usually obtained by a fit routine comparing the measured PTC's with respective PTC's calculated from the applied optical model.

At this point it is already obvious that the number of parameters which can be deduced is limited. By measuring Ψ and Δ in a single wavelength measurement at one angle of incidence and sample orientation, ellipsometry can provide two intrinsic sample parameters. Therefore, it has to be ensured that there is a reasonable sensibility to the parameter of interest. In highly absorbing materials it can happen for instance that the penetration depth of light is so small that the electric field in the layer of interest is already damped too strongly. In anisotropic samples the special case might occur in which the electric field vector of the refracted light inside the sample is almost perpendicular to the optical axis of interest. In both examples the sensibility could be low. By using commercially available fit routines, such problems can be tested by means of the so-called standard error. Finally, it has to be ensured that the parameters of interest are not coupled to each other which happens if both of them change the polarization properties of the sample in the same manner. For example, it is sometimes difficult to measure a layer thickness and it's refractive index independently from each other. In a numerical fit, the parameter coupling can be tested by means of the covariance matrix of the standard errors.

The discussion of restrictions in the second evaluation step should emphasize that qualitative information about the sample structure are essential in order to obtain good quantitative results. Indications for deficiencies in the assumed sample structure are for example unexpected interference signatures or an inconsistent dispersion of a deduced dielectric function.

The simple scheme of Fig. 1.3 does not include the important and sometimes demanding step of the definition of appropriate measurement geometries (angle of incidence, sample orientation, etc.) in order to achieve the best possible sensitivity to the sample parameters of interest. It is often not worthwhile to measure just in all possible configurations (e.g. in the whole accessible angle of incidence range). Configurations with low sensitivity to the parameter of interest (e.g. very high or low angles of incidence) may just increase the error in the final result. Appropriate configuration can be chosen by some simple preliminary considerations. If necessary, these can be subsequently modified in an iterative procedure. Thin films are usually best measured at incidence angles near the Brewster angle of the respective substrate material. In some cases it is more efficient to calculate the best configuration in a preliminary simulation.

Since all other evaluation steps are based on the chosen measurement configurations a final flow chart of an ellipsometric measurement may appear rather complicated (Fig. 1.5). In this resulting scheme the significance of an appropriate optical model becomes again evident. It is important to remember that ellipsometry is initially reference free measuring how a sample changes the polarization of an incident light beam. All subsequently derived parameters depend on the best possible assumption of the sample structure and the validity of the applied optical models. Following Eugene A. Irene, who has brought this into phrase, this means in turn that if the information about the sample structure is insufficient: "Ellipsometry is perhaps the most surface sensitive technique in the universe. However you often don't know what it is you have measured so sensitively".

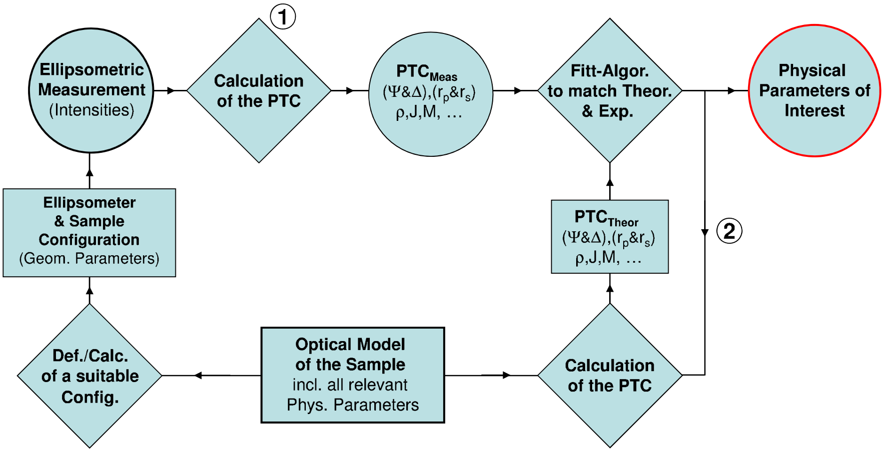

Fig. 1.5 Extended scheme of the data evaluation in an ellipsometric measurement. The two major calculation steps, which can be found already in the simplified representation of Fig. 1.3 are labeled ① and ②

1.3.2 Determination of Ψ and Δ

The determination of Ψ and Δ or the more generalized PTC's of a sample requires some mathematical tools (calculation step ① in Figs. 1.3 and 1.5). First of all a suitable description of polarized light is needed. Furthermore, all optical components including the sample under investigation have to be represented according to their ability to change the state of polarization. These theoretical tools can be finally used to calculate relative intensities which are measured at a detector or, in turn, to determine the PTC's of the sample from the measured intensities.

1.3.2.1 Polarized Light

To simplify the problem as much as possible, assumptions concerning the propagation of light between optical components and the sample are necessary.

- Since linear optical effects are investigated each wavelength λ is addressed separately in a quasi-monochromatic approximation.
- The distances between the optical components are much larger than the wavelength and the coherence length of the light. We can assume planar transversal electromagnetic (TEM) waves propagating only in forward direction from the light source to the detector. In other words, all optical components interact independently, one after another, with the light and interferences between them are avoided. This assumption has to be critical reviewed, e.g. for laser light sources where the coherence length is much larger than for conventional light sources and in near field experiments.

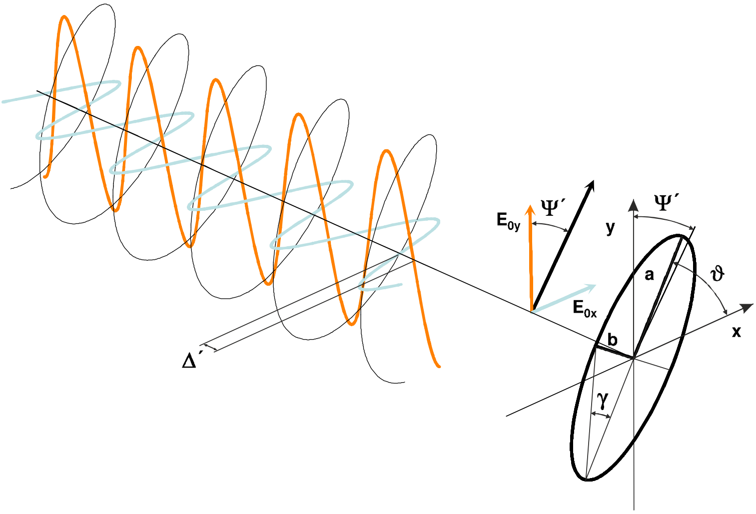

Fig. 1.6 Elliptically polarized light and the projected polarization ellipse. Mathematically the polarization state is defined by three equivalent parameter sets [Ψ'/Δ'—amplitude quotient and phase difference], [ϑ/γ—azimuth angle and ellipticity], and $\chi = 1/\tan\Psi \exp[i\Delta]$

- The surrounding medium is assumed isotropic and homogeneous (air, vacuum, water, etc.). Thereby the polarization state does not depend on the propagation direction and can be separately considered.
- The magnetic susceptibility is constantly one in all optical experiments and the polarization of light is fully described by the electric fields.

For the mathematical description of a polarization one can choose without further loss of generality a Cartesian coordinate system so that the light propagates along the positive direction of the z-axis. A common description of an arbitrarily planar monochromatic TEM wave is then given by

$$\begin{aligned} E_x &= E_{0x}\exp\big[i(kz-\omega t)\big]\exp[i\delta_x], \\ E_y &= E_{0y}\exp\big[i(kz-\omega t)\big]\exp[i\delta_y]. \end{aligned} \tag{1.3}$$

Equation (1.3) represents the general case of an elliptical polarization as illustrated in Fig. 1.6. The wave vector $k = 2\pi/\lambda$ and the angular frequency $\omega = 2\pi\nu$ are connected by the known dispersion relation for TEM waves in transparent media. The orientation of the two perpendicular basis vectors in x- and y-direction is free of choice for the moment. The amplitudes E_{0x} and E_{0y} together with the phases δ_x and δ_y for the x and y component, respectively, define the polarization of the light. This set of information can be merged in a so-called Jones vector [30]:

$$\bar{E}^{Jones} = \begin{pmatrix} E_{0x}\exp[i\delta_x] \\ E_{0y}\exp[i\delta_y] \end{pmatrix}. \tag{1.4}$$

However, the absolute phase is not measurable and the absolute intensity ($I \sim E_{0x}^2 + E_{0y}^2$) is an arbitrary value which is not of interest in an ellipsometric measurement. The polarization state is therefore already fully defined by only two parameters: The relative amplitude $\tan \Psi' = E_{0x}/E_{0y}$ and phase $\Delta' = \delta_x - \delta_y$ of the x and y component. Sometimes these two parameters are combined in a single complex number $\chi = 1/\tan \Psi' \exp[i\Delta']$. Another alternative representation refers to the ellipse, which yields from a projection of the electric field vector to the x–y-plane. The respective parameter pair is given by the azimuth angle ϑ between the main axis of the ellipse and the x-axis and the ellipticity γ (Fig. 1.6). Please note that the parameters Ψ' and Δ', which define here the polarization state of light, are in general not identical with the previously defined Ψ and Δ values, which describe how the sample changes the polarization. Only in the special historically important case, where the incident light is chosen 45° linearly polarized with respect to the plane of incidence, both parameter sets match. Commercially available ellipsometers determine Ψ and Δ independent from the selected incident polarization.

So far, all representations of the polarization are only applicable for totally polarized light. Hence, they represent 100 % linear, circular or elliptically polarized light and the constituting parameter pairs are of a well defined value. Unfortunately, this is sometimes not sufficient and it is necessary to consider also partial polarizations. Possible sources of partial polarized light are

- non ideal polarizers,
- lateral inhomogeneous samples (e.g. rough surfaces/interfaces or inhomogeneous film thickness),
- a divergent light beam (e.g. a short focal distance results in an uncertain angle of incidence),
- an insufficient spectral resolution and broad spectral line width, respectively.

Independent from the inbound polarization and the source of depolarization, partial polarization means that the well defined polarization is replaced by a statistical mixture of different polarization states. In this view the components of the Jones vector are now time dependent and polarization is measurable just as a time-average. A proper description of the partially polarized light requires therefore a third parameter which for example characterizes the probability w to find a certain polarization state. Related to the fact that effective intensities (time-averaged fields) are finally measured, the three constituting parameters are often expressed in terms of intensities. Complemented by the total intensity they form the 4 Stokes parameters [31]:

$$
\begin{aligned}
S_0 &= I, \\
S_1 &= I_x - I_y, \\
S_2 &= I_{+\pi/4} - I_{-\pi/4}, \\
S_3 &= I_l - I_r.
\end{aligned}
\tag{1.5}
$$

The first Stokes parameter contains simply the total intensity I of the light. I_x, I_y, $I_{+\pi/4}$, and $I_{-\pi/4}$ are the intensities, which would pass through an ideal linear