Springer Series in Surface Sciences 52

Karsten Hinrichs
Klaus-Jochen Eichhorn *Editors*

Ellipsometry of Functional Organic Surfaces and Films

Second Edition

Springer

Springer Series in Surface Sciences

Volume 52

This series covers the whole spectrum of surface sciences, including structure and dynamics of clean and adsorbate-covered surfaces, thin films, basic surface effects, analytical methods and also the physics and chemistry of interfaces. Written by leading researchers in the field, the books are intended primarily for researchers in academia and industry and for graduate students.

More information about this series at http://www.springer.com/series/409

Karsten Hinrichs · Klaus-Jochen Eichhorn
Editors

Ellipsometry of Functional Organic Surfaces and Films

Second Edition

Springer

Editors
Karsten Hinrichs
Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V.
Berlin
Germany

Klaus-Jochen Eichhorn
Abteilung Analytik
Leibniz-Institut für Polymerforschung Dresden e.V.
Dresden, Sachsen
Germany

ISSN 0931-5195 ISSN 2198-4743 (electronic)
Springer Series in Surface Sciences
ISBN 978-3-319-75894-7 ISBN 978-3-319-75895-4 (eBook)
https://doi.org/10.1007/978-3-319-75895-4

Library of Congress Control Number: 2018932173

1st edition: © Springer-Verlag Berlin Heidelberg 2014
2nd edition: © Springer International Publishing AG, part of Springer Nature 2018
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Printed on acid-free paper

This Springer imprint is published by the registered company Springer International Publishing AG part of Springer Nature
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Foreword

Given the increasingly important role of spectroscopic ellipsometry (SE) as a real-time, non-perturbing, monitoring, and characterization tool in numerous technological and biomedical applications, the editors, authors, and Springer are commended for publishing the 2nd edition of this monograph, which is dedicated to significant applications of SE to functional organic surfaces and thin films. Retained topics from the first edition cover 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, thin-film organic semiconductors for photovoltaics and light emitters, and recent developments of SE instrumentation and related techniques over an extended optical bandwidth.

New topics that appear in the 2nd edition include SE studies of bonding of biomolecules on self-assembled monolayers, structure and interactions of hydrated polymer thin films, ellipsometry of solvent-induced swelling at soft polymer interfaces, optical properties of anisotropic thin films of organic dye aggregates, relationship between morphology and optical properties of conjugated polymers, and polarons in conducting polymers.

This updated monograph is a welcome contribution to the expanding ellipsometry literature.

New Orleans, USA

R. M. A. Azzam
University of New Orleans

Acknowledgements

The editors would like to acknowledge all authors for their contributions and many valuable discussions, and Arnulf Röseler for his lasting support in helping for understanding of the ellipsometric world. In addition, this book would not have been possible without the motivation and support of our families; KJE thanks his wife Sigrun and his children Susanne and Jörg, and KH thanks his wife Claudia and his daughter Daria. For permanent technical support in the preparation of the book, we are indebted to I. Engler and E. Bittrich.

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

Contents

Part I Biomolecules at Surfaces

Part IV Thin Films of Organic Semiconductors for OPV, OLEDs and OTFT

Part V Developments in Ellipsometric Real-Time/In-situ Monitoring Techniques

Part VI Infared Spectroscopic Methods for Characterization of Thin Organic Films

Part VII Optical Constants

Contributors

Maria Isabel Alonso Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Bellaterra, Spain

Hans Arwin Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden

Dennis Aulich Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Damien Aureau Inst. Lavoisier, CNRS, UMR 8180, University of Versailles St Quentin Yvelines, Versailles, France

Francesco Bisio Istituto CNR-SPIN, Genova, Italy

Eva Bittrich Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Analytik, Dresden, Germany

Lars Bittrich Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Verbundwerkstoffe, Dresden, Germany

Mariano Campoy-Quiles Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Bellaterra, Spain

Maurizio Canepa OPTMATLAB, Department of Physics, University of Genova, Genova, Italy

Loredana Casalis Elettra Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy

Ornella Cavalleri OPTMATLAB, Department of Physics, University of Genova, Genova, Italy

Christoph Cobet Center of Surface and Nanoanalytics (ZONA), Johannes Kepler University Linz, Linz, Austria

Klaus-Jochen Eichhorn Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Analytik, Dresden, Germany

Michael Erber Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Analytik, Dresden, Germany

Norbert Esser Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Dominik Farka Linz Institute of Organic Solar Cells (LIOS), Johannes Kepler University Linz, Linz, Austria

Andreas Furchner Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Michael Gensch Institut für Strahlenphysik/Institut für Ionenstrahlphysik und Materialforschung, Helmholtz-Zentrum Dresden-Rossendorf, Dresden, Germany

Jacek Gasiorowski Center of Surface and Nanoanalytics (ZONA), Johannes Kepler University Linz, Linz, Austria; Linz Institute of Organic Solar Cells (LIOS), Johannes Kepler University Linz, Linz, Austria; EV Group E.Thallner GmbH, St. Florian am Inn, Austria

Ovidiu D. Gordan Semiconductor Physics, Technische Universität Chemnitz, Chemnitz, Germany

Karsten Hinrichs Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Tino Hofmann Department of Electrical Engineering, University of Nebraska–Lincoln, Lincoln, NE, USA

Kenneth Järrendahl Department of Physics, Chemistry and Biology, Linköping University, Linköping, Sweden

Meike Koenig Karlsruhe Institute of Technology (KIT), Institute of Functional Interfaces, Advanced Polymers and Biomaterials, Eggenstein-Leopoldshafen, Germany

Argiris Laskarakis Lab for Thin Films-Nanosystems & Nanometrology (LTFN), Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece

Stergios Logothetidis Lab for Thin Films-Nanosystems & Nanometrology (LTFN), Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, Greece

Michele Magnozzi OPTMATLAB, Department of Physics, University of Genova, Genova, Italy

Nico B. Eisele Biosurfaces Unit, CIC BiomaGUNE, Donostia, San Sebastian, Spain; Department of Cellular Logistics, Max Planck Institute of Biophysical Chemistry, Göttingen, Germany

Thomas W. H. Oates Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Wojciech Ogieglo Advanced Membranes and Porous Materials Center, 4700 King Abdullah University of Science and Technology (KAUST), Thuwal, Kingdom of Saudi Arabia

Pietro Parisse Elettra Sincrotrone Trieste S.C.p.A., Basovizza, Trieste, Italy

Simona D. Pop Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Ralf P. Richter Biosurfaces Unit, CIC BiomaGUNE, Donostia, San Sebastian, Spain; Department of Molecular Chemistry, J. Fourier University, Grenoble, France; Max Planck Institute for Intelligent Systems, Stuttgart, Germany; School of Biomedical Sciences, University of Leeds, Leeds, UK

Jörg Rappich Inst. für Si-Photovoltaik, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

Charles Rice Department of Electrical Engineering, University of Nebraska–Lincoln, Lincoln, NE, USA

Keith B. Rodenhausen Department of Chemical and Biomolecular Engineering, University of Nebraska–Lincoln, Lincoln, NE, USA

Katy Roodenko Department of Materials Science and Engineering, Laboratory for Surface and Nanostructure Modification, University of Texas at Dallas, Richardson, TX, USA

Daniel Schmidt Department of Electrical Engineering, University of Nebraska–Lincoln, Lincoln, NE, USA

Eva Schubert Department of Electrical Engineering, University of Nebraska–Lincoln, Lincoln, NE, USA

Mathias Schubert Department of Electrical Engineering and Center for Nanohybrid Functional Materials, University of Nebraska-Lincoln, Lincoln, NE, USA

Ilaria Solano OPTMATLAB, Department of Physics, University of Genova, Genova, Italy

Philipp Stadler Linz Institute of Organic Solar Cells (LIOS), Johannes Kepler University Linz, Linz, Austria

Guoguang Sun Leibniz-Institut für Analytische Wissenschaften – ISAS – e.V., Berlin, Germany

Peter Thissen Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany

Martin Tress Institut für Experimentelle Physik II, Universität Leipzig, Leipzig, Germany

Petra Uhlmann Leibniz-Institut für Polymerforschung Dresden e.V., Abteilung Nanostrukturierte Materialien, Dresden, Germany

Sylvia Wenmackers Faculty of Philosophy, University of Groningen, Groningen, The Netherlands

Florent Yang Institute for Heterogeneous Material Systems, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

Dietrich R. T. Zahn Semiconductor Physics, Technische Universität Chemnitz, Chemnitz, Germany

Xin Zhang Institut für Silizium Photovoltaik, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany

Introduction to Book Contents

For more than a century, ellipsometry has been utilized by physicists as a nondestructive, absolute, and thin-film-sensitive optical method to determine index of refraction and absorption of solid materials (metals, semiconductors, and oxides). Over the last few decades, user-friendly ready-to-use ellipsometers with application-related accessories 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 characterization of superconductors and metamaterials, rough and nanostructured surfaces, complex hybrid films, and plasmonic and magneto-optic samples. [1–3] 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, beyond thickness determination 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 biomolecules. The analysis of functional surfaces often requires new methods to apply ellipsometry for quantitative, nondestructive, 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 emphasize 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, when the probing wavelengths are in the range of structure dimensions, the measured spectra cannot be sufficiently understood within homogeneous layer optical models. For such cases, in particular, promising attempts have been made in combination with numerical simulations (as e.g., rigid coupled wave analysis and finite-element calculations) but also scatterometric as well as Mueller Matrix ellipsometry measurements. Beside these approaches in general, the structural and anisotropic properties over several length scales down to the μm and nm range are of high relevance for thin films and surfaces in many sensoric, opto-electronic, and biomedical applications. With respect to laterally higher resolved measurements, recent methodical developments for ellipsometric- and polarization-dependent measurements in the infrared spectral range are addressing to involve tunable lasers, microfluidic, and near-field measurement concepts.

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 noncontact and nondestructive 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 24 chapters grouped in seven parts, 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.

The first edition of this book having 18 chapters was published as print book and eBook in 2014. It was very successful in the community, e.g., it was one of the top 25% most downloaded eBooks in the relevant SpringerLink Collection. So, we decided in agreement with Springer to publish a revised and extended second edition.

Therefore, we present in the second edition beside some chapters in their original form a lot of updated, improved chapters as well as complete new ones:

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.

M. Canepa et al. demonstrated recently that spectroscopic ellipsometry in combination with AFM nanolithography is able to characterize ultrathin self-assembled monolayers and their interaction with biomolecules on surfaces. Analyzing the difference spectra, they describe an in situ hybridization process.

"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). This chapter is complemented now with a new method for a more precise ellipsometric determination of T_g developed by E. and L. Bittrich.

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 actual chapter also, enzymes are included. During the last years, in situ Infrared spectroscopic ellipsometry (IR-SE) comes more and more into play to characterize molecular and supermolecular changes at solid–liquid or solid–gaseous interfaces. A. Furchner shows impressively that in situ IR-SE can provide a lot of information on the structure and interactions in hydrated polymer films with focus on new data on hydrogen-bonding phenomena. The second new contribution in the polymer topic is given by W. Ogieglo. He reviews the important recent developments in the application of ellipsometry in industrial membrane-related studies. Sorption, transport, and penetrant-induced phenomena in membrane-relevant thin films exposed to organic solvents or high-pressure gases are discussed.

In the first chapter of the 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 second part, complicated nanostructured (sculptured) thin films with high anisotropy are presented by K. B. Rodenhausen et al. These highly ordered three-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 shown in the last updated 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. In a new chapter by K. Roodenko and P. Thissen, details on thin films formed by organic dye aggregates are given. They present data on the optical properties obtained by Vis ellipsometry and polarized infrared spectroscopy. New as well is the chapter of M. I. Alonso and M. Campoy-Quiles on conjugated polymers. They discuss the relationship between the morphology and optical properties of these polymers and their blends with fullerenes. The last contribution in this topic given by C. Cobet et al. is concerned with polarons in conducting polymers. The authors use spectroscopic ellipsometry and ATR-IR to study the formation of polarons in chemically and electrochemically doped polymers.

"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 provides fascinating insights into the chemistry of thin organic films as described by J. Rappich et al. Current results on IR-SE investigation of the maleimidobenzene modified Si surfaces are included now. And last but not least, it is possible to use SE for the inline quality control of organic thin-film fabrication on rigid and flexible substrates. In their part of Chap. 19, S. Logothetidis and A. Laskarakis give an overview on the state-of-the-art in this field.

Infrared ellipsometry (IR-SE) but also other surface-sensitive FTIR spectroscopic methods for the characterization of thin organic films are reviewed by K. Roodenko et al. in Chap. 21. 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. 22, M. Gensch presents the technical background and interesting applications and outlook.

This book is of great interest to anyone who would like to use spectroscopic ellipsometry to study thin organic films of polymers or small molecules to have an idea on their material optical constants. Thus, the last chapter of the book provides support in this direction: D. Aulich and A. Furchner 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.

Karsten Hinrichs
Klaus-Jochen Eichhorn

References

1. H.G. Tompkins, E.A. Irene (eds.), Handbook of Ellipsometry (Springer, 2005)
2. H. Fujiwara (ed.), Spectroscopic Ellipsometry: Principles and Applications (Wiley, New York, 2007)
3. M. Losurdo, K. Hingerl (eds.), Ellipsometry at the Nanoscale (Springer, Berlin and Heidelberg, 2013)

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

---

C. Cobet (✉)
Center for Surface- and Nanoanalytics, Johannes Kepler
Universität Linz, Altenbergerstrasse 69, 4040 Linz, Austria
e-mail: christoph.cobet@jku.at

K. Hinrichs and K.-J. Eichhorn (eds.), *Ellipsometry of Functional Organic Surfaces and Films*, Springer Series in Surface Sciences 52,
https://doi.org/10.1007/978-3-319-75895-4_1

in many different application fields. Accordingly, a couple of books, book chapters, 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. 1.2a). 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.

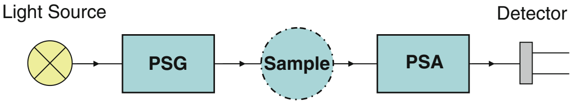

Fig. 1.1 Principle concept of ellipsometric and polarimetric techniques. The Polarization State Generator (PSG) and Polarization State Analyzer (PSA) may consist of a polarizer or a combination of a polarizer and retardation component

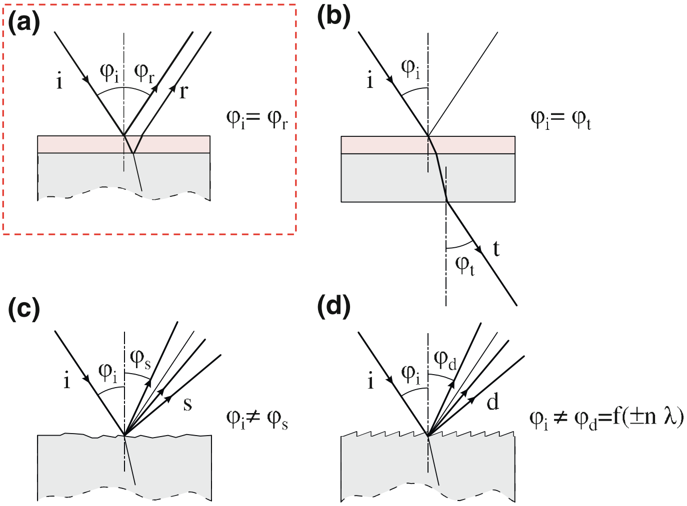

Fig. 1.2 Fundamental interaction of incident light on different samples under an angle φ_i: **a** reflection, **b** transmission, **c** scattering, and **d** diffraction. All introduced ellipsometric problems are reflection measurements (*red dashed box*)

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 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. 1.2b–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 1800s 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

---

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

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].

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

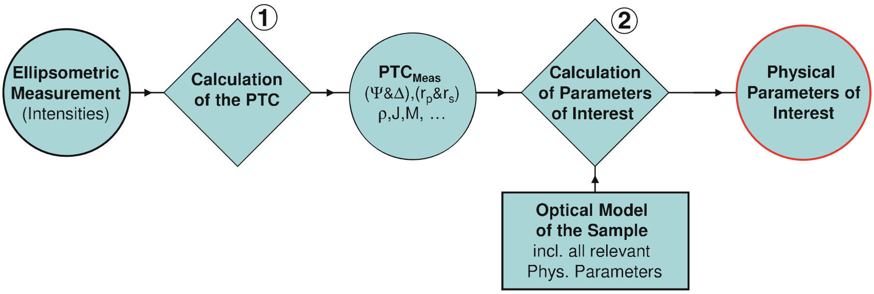

Fig. 1.3 Basic data evaluation steps in an ellipsometric measurement. The *left hand side* of the flow chart depicts the determination of the polarizing properties of the sample which are represented e.g. by the ellipsometric angles Ψ and Δ or in more general by polarization transformation coefficients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