

# 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.

## References

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