Preface

"*Light has a relation to the matter which it meets with in its course, and is affected by it, being reflected, deflected, transmitted, refracted, and absorbed by particles very minute in their dimensions. At present the most instructed persons are, I suppose, very far from perceiving the full and close coincidence between all the facts of light interacting with particles and the physical account of them which the theory supplies.*" This is how Michael Faraday started his "Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light" published in 1857 in the Philosophical Transactions of the Royal Society. More than a century and a half has passed, and despite the enormous advances in understanding the interaction of light with nanostructured materials, this sentence still expresses a way of thinking common to those who enter the world of physical investigations of the nature and action of a ray of light with nanostructures that were of the order of "*1/282000th of an inch*", which we say 35 nm nowadays!

Therefore, the term nanotechnology is new, but research at the nanometer scale is not new at all!

Richard Feynman's renowned lecture "There's plenty of room at the bottom" (1959 at Caltech) is seen as the milestone of nanoscience. Noteworthily, Feynman also presciently recognized the synergy between the ability to make things smaller and the ability to see and probe what has been made as the key to progress in the field of nanoscience and nanotechnology.

Indeed, almost 15 years earlier, in 1945, Alexandre Rothen made the pioneering statement that "*during the course of an investigation of the reaction between films of antigens and antibodies, it was found that an apparatus was needed which would measure film thickness rapidly and with an accuracy of at least* 1 Å" (which is a fraction of a nanometer!). The apparatus that was devised was given the name "ellipsometer" [1]. Already in 1945, the ellipsometer was capable of measuring a film thickness to within ±0.3 Å!

Therefore, we could say that ellipsometry was pioneering nanoscience, where both light and matter play leading roles.

In the past few years, entirely new classes of materials have been discovered and developed. These include one-dimensional nanowires and quantum dots of various compositions, polyvalent noble metal nanostructures, graphene, metamaterials, superlattices, and a wide variety of other nanoparticle assemblies. A toolbox of nanostructures is being engineered with tailored, functional optical properties and colors for optics, photonics, and biomedical applications ranging from therapeutics to diagnostics. The need for a wider understanding of nanoparticle and nanostructures exploiting characterization techniques down to the level of 0.1–100 nm is the driving force of significant changes in optical metrology, since, from the optical point-of-view, the interaction of materials with photons is strongly dependent not only on the chemistry but also on structure, size, and shape, which can then be used to control light propagation.

The versatile nature of ellipsometry as a functional, nanoscale sensitive, and nondestructive technique, is paving the way for the application of these new nanostructures in a widening field of technologies and for breakthroughs in knowledge of thin film multilayer surfaces, composite and smart materials, and materials engineering at the nanoscale.

Scope of the Book

The primary aim of this book is to present and introduce ellipsometry in nanoscience and nanotechnology making a bridge between the classical and nanoscale optical behavior of materials. The progress in the current understanding of optical properties of nanomaterials is an important driving force for developing a variety of applications.

This book helps to delineate the role of the nondestructive and noninvasive optical diagnostics of ellipsometry in improving science and technology of nanomaterials and related processes by illustrating its exploitation ranging from fundamental studies of the physics and chemistry of nanostructures to the ultimate goal of turnkey manufacturing control.

This book is written for a broad readership: materials scientists, researchers, engineers, as well as students, and nanotechnology operators who want to deepen their knowledge about both basics and applications of ellipsometry to nanoscale phenomena. Readers might have quite different backgrounds, interests, and understanding of optics, physics, materials, and of their properties and technologies, and, despite the difficulty of having a single book addressing a varied audience, we have at least one chapter of interest to everyone!

Therefore, this book goes through different levels. It starts as a general introduction for people curious to enter the fields of ellipsometry and polarimetry applied to nanomaterials and progresses to articles by experts on specific fields that span from plasmonics, optics, to semiconductors and flexible electronics. The core belief reflected in this book is that ellipsometry applied at the nanoscale offers new ways of addressing many current needs.

The book also explores forward-looking potential applications. The potential of ellipsometry is not yet fully used, and it is currently the only optical technique which can reliably provide phase information. Especially, the phase is sensitive to e.g., minute changes in the thickness of overlayers, or adsorbates or structural changes in nanomaterials. The competing interferometric measurements still lack solutions to the problems of being constrained to normal incidence, of managing the dispersion of the optical components and also vibrational control.

The question is: how to move forward?

The intrinsic difficulty of ellipsometry in nanotechnology is that it is a multidisciplinary field involving optics; therefore, chemists, physicists, material scientists, engineers, molecular biologists, pharmacologists, etc., should all be familiar with the basic optics concepts in those heterogeneous fields, which is sometime not straightforward.

Therefore, the goal was not to write a monograph style book, and even less a textbook, but a book with contributions from multidisciplinary fields, with different approaches and languages that different readers with optic vocabularies imbibed in their scientific infancy can become acquainted with. The principles of ellipsometry are not always seen as easy. For many researchers, the lack of knowledge on polarized light and on the Maxwell equations—with specific boundary conditions, especially for nanomaterials—make spectroscopic ellipsometers seem mystic devices, providing (pseudo-)dielectric functions. Furthermore, the meaning of the ellipsometric measurables Ψ and Δ may not be straightforward and modeling procedures are required to derive the dimensional and optical properties of the materials. Therefore, the primary goal of this book is to provide a common ground for a better understanding of how to use ellipsometry effectively. The position reflected in this book is that this goal can only be accomplished by materials scientists, optics scientists, process engineers, and nanotechnology analysts exchanging background and expertise and working together on a found basis.

Excellent books on the fundamental of ellipsometry already exist and for more detailed description of the principles of polarized lights and ellipsometry the reader is referred to the books "*Ellipsometry and Polarized light*" edited by R. M. A. Azzam and N. M. Bashara, "*Handbook of ellipsometry*" edited by H. G. Tompkins and E. A. Irene.

Organization of the Book

This book captures the interdisciplinary nature of nanoscience and provides a balanced approach to introduce the principles of ellipsometry and exploit them in various fields serving as both an education and training text and as a reference point for research and development providing the following unique features:

- A unifying vision of ellipsometry merging nanotechnologies, including ellipsometry instrumentation and modeling best practice, fabrication processes, nanomaterials, applications, and technologies

- A full perspective about the various information that can be gained depending on the spectral range and ellipsometry configuration (from the Terahertz to near-infrared, visible and far-UV)
- A multifaceted study of novel chemical, electrochemical, and optical phenomena in nanostructures
- A coverage of inorganic and organic semiconductor nanomaterials, superconductors, biomaterials, and nanocomposites, as well as graphene optically characterised by ellipsometry
- A focus on new technologies based on the interaction of light with nanomaterials such as *plasmonics and metamaterials*
- A coverage of ellipsometry in bioresearch and medicine
- A critical and comprehensive assessment of ellipsometry in the industry and in the market place, with future forecasts.

We took care of organizing this book and sorted and clustered the contributions with respect to topics without trying to squeeze all authors into a common frame. The story is not only about the things; it is also about the people! It is peoples' background and language that make them communicative. Therefore, because of multidisciplinarity of nanoscience, each author wrote each chapter in a self-standing way, certainly referring to other chapters, but the nomenclature has not been unified all over the book.

Therefore, as the Editors of this book, we are deeply grateful to all contributing authors for their efforts and their willingness to share recent results within the framework of "nanoscience and nanotechnology". We are especially proud that the authorship includes pioneers and newcomers to this intriguing and fertile field of research. With chapters addressing fundamental and practical questions of physics, chemistry, quantum theories, and real-time monitoring of fabrication processes related to nanostructures, this book shows the reader how ellipsometry can help to achieve a better orientation in nanoscale optical phenomena.

Most readers will use the book to get a solid grasp of the fundamentals, so that they can move on to more complex topics. Some of the chapters can be read independently of the others, on the assumption that the fundamental in Chaps. 1–5 have been fully assimilated. The reader is just left to be driven by his/her curiosity and interests!

Therefore, Chap. 1 has been devoted to introducing the main concepts of the ellipsometry technique and its historical context, also related to nanomaterials. This book does not presuppose that the reader has a working knowledge of ellipsometry, therefore a beginner can grasp the fundamentals needed in this chapter.

Chapter 2 takes the fundamentals a bit further, letting the reader become more confident with the polarimetric properties of a sample and, consequently, moving from standard ellipsometry to generalized ellipsometry and Mueller polarimetry; it also deals with the instrumental aspects of ellipsometry and polarimetry, giving a perspective on "how" ellipsometry and polarimetry measure what they measure. Recent developments exploiting Mueller polarimetry in fields as diverse as sub-wavelength grating metrology and cancer detection in biomedicine are discussed.

The book then turns to fundamental optical properties and modeling advances needed to explore the nanoscale and to application-oriented considerations. Therefore, Chap. 3 is dedicated to the optical properties of materials consisting of a matrix with inclusions and layered materials. Various *effective medium theories* (EMAs) are available, the result of which is the so-called "effective dielectric function" that describes the macroscopic optical response of a heterogeneous system. Both strengths and weaknesses of the various EMAs are described in this chapter.

One of the most common applications of EMAs is the analysis of surface roughness from ellipsometric spectra. Surfaces and interfaces are also important in explaining nanomaterials' behavior. In bulk materials, only a relatively small percentage of the atoms will be at or near a surface or interface. In nanomaterials, half or more of the atoms are near interfaces and at the surface. Therefore, a critical review of major results in describing surface roughness with effective medium theories is presented in Chap. 4.

Chapter 5 extends the discussion on EMAs to plasmonic materials and introduces the "plasmonics" cluster of chapters that extends from Chaps. 5–9. The fundamental relationship between the dielectric function, ellipsometry, and plasmonic materials is given in Chap. 5, while Chap. 6 enters into the details of the optical characterization of substrate-supported nanostructured noble metal nanoparticles, extending the discussion on the validity of EMAs to the Thin Island Film theory. With Chap. 7, which presents a review of fabrication, modeling and characterization aspects related to the fascinating field of metallic periodic nanostructures, we extend the discussion also to metamaterials. Chapter 8 overviews the merging of Mueller polarimetry and rigorous coupled wave analysis, described in details in the previous chapter, for the analysis of periodic nanostructures. Chapter 9 deals with magnetic plasmonic nanocomposites giving some examples of applications of magneto-optical Kerr spectroscopy.

Chapter 10 interrelates the discussions of the different aspects of standard ellipsometry, generalized ellipsometry, and Mueller polarimetry to the measurement and analysis of exotic and fascinating shapes of biaxial nanostructures. A complete discussion on the appropriateness of generalized ellipsometry for the determination of principal optical constants of chiral and achiral multifold and helical sculptured thin films is given.

Extending the spectral range to Terahertz ellipsometry is the innovative subject of Chap. 11, since there exists a wealth of fascinating excitation mechanisms with eigenfrequencies in the THz domain in condensed and soft matter, such as spin transitions, collective modes of biological molecules, local free charge carrier oscillations, dynamic motion of magnetic domains, ferroelectric domains, or collective charge phenomena, which are discussed here as examples.

Chapter 12 focuses on infrared ellipsometry, which is proven to be a powerful technique for the studies of electronic excitations and lattice vibrations in both the normal and superconducting states and, therefore, for highlighting superconducting phenomena in nanomaterials.

Exploiting light in the NIR–VIS–UV spectral range, which is common to all commercial ellipsometers, to probe in real-time various nanoscale phenomena at surfaces and interfaces is the subject of Chaps. 13 and 14. Many nanoscale characterization methods cannot probe samples in native or desired operating (*operando*) environments. Enabling nanoscale materials real-time analysis under realistic conditions is a critical need. Chapter 13 reviews the application of real-time ellipsometry to probe charge transfer processes in surface-nanoparticle—molecule coupled systems of interest for photonics, molecular electronics and sensing, while the detection of phenomena and kinetics occurring at the solid–liquid interface, which is an important field in electrochemistry, is overviewed in Chap. 14.

Having learned that ellipsometry has all the hardware, instrumental setups, and modeling capabilities to address the process-nanostructure—optical properties interrelationship, a series of examples of the exploitation of ellipsometry in research and industry of both organic and inorganic semiconductors is given in the cluster of Chaps. 15–19.

One possible strategy toward functional optoelectronic composites for OLEDs and organic flexible solar cells is to use an organic material that can efficiently harness photons from light and convert them to useful energy. Therefore, issues related to the optical characterization of organic, polymeric layers combined with inorganic materials are reviewed in Chap. 15.

Another domain that emerged two decades ago and which is another hot topic, concerns the optical properties of quantum structures to make biological tags, efficient light emitting diodes (LEDs), efficient solar cells, or low-consumption flat panel displays. The semiconductor industry is also working on materials for "beyond CMOS" devices. Graphene is the most prevalent example of this. Ellipsometry applied to the analysis of graphene is discussed in Chap. 16 while Chap. 17 focuses on semiconductor nanocrystals.

We then turn to industrial quality control: Spectroscopic ellipsometry is the only method that can be used to measure inline multiple thicknesses on fully fabricated CMOS chips on a test area of 50 x 100 μm. One of the advantages of this technique is that standard uncertainty values of the thickness found using SE are typically between 0.01 and 0.05 nm and, therefore, considerably less than those found with the other electrophysical techniques. Therefore, inline applications of ellipsometry to the semiconductor industry are presented in Chap. 18.

Chapter 19 looks at industry and market perspectives, concluding with presenting capabilities and ideas for exploiting ellipsometry in several industries.

Chapter 20 offers a broad perspective of the concept that "the ideal" characterization tool for nanomaterials does not exist, but corroborating techniques must be used. Therefore, this chapter shows how ellipsometry can corroborate, and be corroborated by, other characterization techniques. Most commonly used structural and chemical characterization methods are introduced to corroborate ellipsometry. Structural characterization methods include scanning or transmission electron microscopies (SEM/TEM), and atomic force or scanning tunneling probe microscopies (AFM/STM). Chemical characterization methods include electron spectroscopies (XPS).

We conclude with Chap. 21 analyzing the influence and the role that nanomaterials and nanotechnologies might or might not effectively play in the *fuzzy* future. This chapter reflects the perspective of nanotechnologists and market-product developers—a perspective that it would be well worth for scientists and engineers interested in fundamental knowledge as well as in applications of nanomaterials to know about.

This book is timely in proposing the state-of-the-art ellipsometry applications to nanomaterials and pointing the way to further exciting developments. We are just at the transition from the first foundational phase of nanotechnology (2001–2010), which was focused on interdisciplinary research at the nanoscale, on the discovery of new phenomena, properties, and functions at the nanoscale, and on the synthesis of a library of components as building blocks for potential future applications, tool advancement, to the second phase (2011–2020), which will be focused on nanoscale science and engineering integration, projected toward direct measurements with good time resolution and science-based design of fundamentally new products.

The transition from the Nano-1 to the Nano-2 phase is focused on achieving direct measurements at the nanoscale, and science-based design of nanomaterials and nanosystems. It is in this context that ellipsometry, with its nondestructive real-time capability of monitoring processes and tailor materials characteristics can play a role in the general purpose of science and technology integration!

Therefore, the Editors hope to contribute with this book to a wider use of ellipsometry in the nanomaterials community, since it is our common vision and experience as a chemist (*ML*) and as a physicist (*KH*) that many questions/problems/issues can be tackled with this technique.

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