Preface

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Thin films have become an important branch of materials science and technology over the last few decades. A thin film is considered in this book as having a thickness between about 1 nm and some 10 µm. Their first application was probably in the field of decorative coatings, but in the last century many other applications in microelectronics, optics, data storage, sensorics, protection and other purposes have had a large impact on the development of thin films and related deposition techniques. Figure 1 displays a variety of thin-film applications from the areas mentioned. Depending on the intended application, thin films are made of metals, inorganic compounds, organic compounds or from biological molecules. The task of the thin-film developer is easily described by stating that the deposition process has to be optimized such that the arrangement of atoms enables the film to fulfill the intended functionality.

Since structure and function are intimately related properties in any material, the characterization of structural properties is a very relevant issue in thin-film development. This book is concerned with the structural analysis of thin films by x-ray scattering procedures. There exist various other characterization techniques like electron microscopy, scanning tunneling methods, ion beam scattering, magnetic resonance, optical spectroscopy and others by which important structure properties may be elucidated. Here, however, the focus is on x-ray scattering. The suitability of this technique for thin-film analysis is mainly motivated by two reasons:

1. The wavelengths of x-rays are of the order of atomic distances in condensed matter, which especially qualifies their use as structural probes.
2. X-ray scattering techniques are nondestructive and leave the investigated sample or – more importantly – the produced device intact.

Electron microscopy might be considered of comparative importance for the characterization of structure and morphology. This technique is a complementary one to x-ray scattering, since it probes a rather confined volume of the sample, whereas x-ray scattering yields information from a much larger volume. Therefore, some micrographs from electron microscopy will appear in the text, but the reader is referred to the special literature for an introduction to the subject.
Various examples from thin film applications: (a) decorative coatings on metal dials, (b) scanning electron micrograph of cross-section from SiGe:C heterojunction bipolar transistor, (c) schematic of SiGe:C BiCMOS architecture with four metal layers, (d) processing of window glass for optical coating (Fotograf: Rainer Maier, BFF, Wittmar), (e) identity card with optical data storage made from bacterial purple membrane containing the protein bacteriorhodopsin and example of stored pixel patterns, (f) cemented carbide cutting insert with c-BN protective coating and (g) tip of a diamond-coated abrasive pencil of 60 µm diameter (figures kindly provided by (a, d, f and g) Fraunhofer IST, Braunschweig [1], (b, c) IHP, Frankfurt (Oder) [2], (e) Prof. N. Hampp, University of Marburg [3]).
This book is intended to give overviews of the relevant x-ray scattering techniques for thin-film work and to equip scientists and engineers with the basic understanding to apply them. It has to be emphasized that for each x-ray technique presented in one of the following chapters there are authoritative and comprehensive textbooks available; these are listed at the end of each chapter and the reader is referred to them for further consultation. It seems, however, that there exists a gap between the highly developed and complex structural sciences on the one hand and the daily needs of materials scientists on the other. Many of the conclusive, effective and powerful techniques that have been developed for structural investigations appear to be not as extensively used in thin-film technology as they would deserve. It is the aim of this book to bridge this gap by introducing the concepts of x-ray techniques that appear most interesting to elucidate the close relations between structure, function and growth of thin films.

Chapter 1 introduces the basic phenomenon of x-ray diffraction by a crystalline lattice. In Chapter 2 methods for the identification of chemical phases are presented. Chapter 3 is related to the line profile analysis of diffraction peaks with respect to film microstructure. Measurement geometries characterized by a grazing incident x-ray beam are introduced in Chapter 4. The preferred orientation of crys-
tallites and residual stresses in thin films are dealt with in Chapters 5 and 6, respectively. Up to this point mostly polycrystalline films will be considered and use will be made of the kinematic theory only. Epitaxial thin films are in the focus of Chapter 7, where high-resolution x-ray diffraction is outlined and the first grounding of dynamical theory is introduced. The majority of the material presented is based on the physical phenomenon of diffraction, but some parts – as for instance the presentation of reflectometry in chapter four – are related to the more general phenomenon of x-ray scattering. This is the reason for the title of the book.

It is recommended to start reading with Chapters 1 and 2, which might be helpful even for those readers to whom the basics are already known in order to become familiar with the conventions and notation used. After this introductory training the reader may consult any other chapter presenting the method that might be expected of relevance for his or her actual work. The emphasis of the book is on x-ray scattering with laboratory setups in contrast to synchrotron radiation beam lines. However, many of the measurement concepts presented are equally realized at synchrotron facilities and may also be applied in experiments with the much higher intensity available at synchrotron sources.

Two concepts or quantities meander through the following chapters like a thread through the tows of the former British royal navy (“roter Faden” [4]). The first of these quantities is the scattering vector that is abbreviated by $Q$ here. The scattering vector is met in almost every chapter since interatomic distances are probed by diffraction only along the direction of $Q$. Diffraction or scattering experiments may be considered as intensity mappings under complex rotations of the sample with respect to the scattering vector. These reorientations are dealt with by the use of three reference frames $\{l_i\}$, $\{s_i\}$ and $\{c_i\}$, one for each frame of the laboratory, the sample and the crystallographic unit cell. The different frames are sometimes confusing for the newcomer to the field. It is recommended that when one seems of having lost the “roten Faden” it might be taken up again by answering the question “what are the coordinates of the scattering vector $Q$ within the respective reference frame?”

The second recurring quantity is that of the x-ray attenuation coefficient $\mu$. In condensed matter x-rays are attenuated on a length scale of some 10 to some 100 µm. These penetration depths are accordingly often larger than the film thickness $t$ and special methods have been developed to restrict the probing beam to the sample volume. In almost all of the forthcoming chapters we have to derive how the $\mu t$ product affects the measured scattering intensities. It may even be stated that the $\mu t$ product can be regarded as the central physical quantity in thin-film analysis by x-ray scattering.

The chapters end with an application section, where studies and works related to the issue of the chapter are presented. The selection of these examples and those mentioned in the main body of the text is probably highly selective and reflects the interest and working areas of the author(s). Since each chapter covers a large field of research activities it was hardly possible to overview fully the many interesting x-ray scattering investigations that have been carried out in the appropriate areas. A collection of exercises is given at the end of each chapter, by the solution of which
the reader may verify the understanding of the text. Solutions to the exercises can be found on the internet [5].

Two further issues are considered in parallel with the main text. These are related, firstly, to the instrumentation in x-ray scattering experiments and, secondly, to the structure of selected material classes. In the instrumentation boxes, the instrumentation required by the experiments described in the chapter is detailed. The structure boxes present crystallographic structures, structural parameters and selected physical properties of relevant materials. The material systems have been chosen in accordance with their relevance to illustrate the x-ray scattering technique in the chapter. The selected material systems are in order of increasing chapter number metals, semiconductors, nanocomposites, optical thin films, dielectric and superconducting materials, hard coatings and finally semiconductors for micro- and optoelectronics. Other combinations would have equally been possible.

Two remarks have to be made on notation: (a) SI units have been used throughout the text and (b) it has been endeavored to use a consistent notation throughout the text. However, this turned out a difficult task, since every chapter covers a highly developed subfield of x-ray scattering with its own nomenclature. It could thus not be completely avoided to make use of the same symbol with different meaning in different chapters. These cases will explicitly be pointed out. In case of doubt, the appropriate meaning of a symbol can be identified by consulting the symbol list.

In some cases, the names of inventors or scientific pioneers are mentioned. It should be borne in mind, however, that scientific achievements always rely on the communication among different researchers exchanging their ideas and imaginations. This statement is illustrated by the famous discussion between P.P. Ewald and M. Laue that laid the basis for the first x-ray diffraction experiments by Friedrich, Knipping and Laue [6]. Scientific progress has always been based on teamwork, even if the protagonists did not know each other personally. This fact is explicitly stated here, since we cannot be sure in every case that all the researchers that should be credited were adequately indicated when one or more of them are mentioned. Since x-ray diffraction is about 100 years old, it may be possible that future research in the history of science will reveal personal contributions of which we were not fully aware at the time of writing. The reader interested in the early history of x-ray diffraction is referred to a paper collection published for the International Union of Crystallography [7].

This book project would not have become reality without the help of some friends and colleagues. Firstly, I would like to thank Paul Fewster and Christoph Genzel for their co-authorship of Chapters 6 and 7. They both agreed on being co-authors to chapters they would be much more qualified of writing themselves and let me assume the role of the first author in order to maintain consistency with the rest of the book. Their great expertise in the respective fields helped enormously to formulate these two state-of-the-art chapters. I enjoyed the work with both of them very much. I am indebted to Daniel Chateigner, Carl Krill, Paolo Scardi, Thomas Schröder, Antonella Tagliente, Mark Vaudin, Thomas Wieder, Don Williamson, Joachim Woitok and Peter Zaumseil, who carefully red draft versions of single chapters, gave valuable recommendations and pointed me to some examples from
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References

Monographs, conference proceedings and internet sites of general relevance

International Union of Crystallography: www.iucr.ac.uk.
Proceedings of the annual Denver X-Ray Conferences (DXC) published by the International Center for Diffraction Data (ICDD)

Special papers