Preface

During the last 20 years interest in high-resolution x-ray diffractometry and reflectivity has grown as a result of the development of the semiconductor industry and the increasing interest in material research of thin layers of magnetic, organic, and other materials. For example, optoelectronics requires a subsequent epitaxy of thin layers of different semiconductor materials. Here, the individual layer thicknesses are scaled down to a few atomic layers in order to exploit quantum effects. For reasons of electronic and optical confinement, these thin layers are embedded within much thicker cladding layers or stacks of multilayers of slightly different chemical composition. It is evident that the interface quality of those quantum wells is quite important for the function of devices.

Thin metallic layers often show magnetic properties which do not appear for thick layers or in bulk material. The investigation of the mutual interaction of magnetic and non-magnetic layers leads to the discovery of colossal magnetoresistance, for example. This property is strongly related to the thickness and interface roughness of covered layers.

The properties of supramolecular structures made from organic thin films can differ entirely from those of individual layers. Supramolecular structures can be composed by amphiphilic layers, for example, which have the capability for lateral self-organization. Particular head groups are attached to these molecules to give them proper functionality. These layers are separated by layers of another material either carrying a second functionality or simply for spatial separation of the first kind of layers. The different sublayers can exhibit different degrees of perfection and crystallinity.

Thin layers and multilayers can be grown using molecular-beam-epitaxy (MBE) or metal-organic-vapor-deposition epitaxy (MOVPE), for example. Layer-by-layer deposition of particular semiconductor material allows for the composition of tailored stacks of sublayers with monolayer and submonolayer accuracy. The functionality of the respective devices requires perfect lattice matching between the sublayers and smooth interfaces. Under conditions of crystal growth, several real-structure effects appear that may reduce the efficiency of the electronic or optoelectronic device. For example, coherent hetero-epitaxy of highly mismatched material combinations is possible only up to a critical layer thickness only. When the thickness increases, misfit dis-

locations are created at the interfaces in order to reduce the strain energy of the system. Another process of relaxation is the growth of strain-reduced islands, which disturbs the smoothness of interfaces. In order to prevent this, slightly misoriented substrates are used, and the epitaxy provides terraces, i.e., locally smooth but macroscopically rough interfaces. Additionally, the statistical character of the growing process gives rise to various local fluctuations of the layer thickness and to waviness of the interfaces on a mesoscopic and nanoscopic scale.

Nowadays the Stranski-Krastanov growth process is used especially to create quantum dots. Here, the growth switches from layer-by-layer into an island-like growth mode. The dots can show quantum size effects which can be used for exciting a particular emission wavelength or reducing the laser threshold of an optoelectronic device. Unfortunately, these dots can hardly be arranged in an ordered array and are still not monodisperse in size, which requires the use of statistical methods of data evaluation. Ordered arrays of lateral nanostructures can be obtained by selective etching of semiconductor quantum-well structures or metallic multilayers, respectively. Because the distance of the defined surface dots or stripes is of the order of several 10–100 nm, this technological process defines a one- or two-dimensional mesoscopic lattice which is best accessed by the x-ray scattering process.

Metallic layers are often prepared using sputtering techniques. In contrast to MBE, this process runs far from thermodynamic equilibrium and the deposited films sometimes become amorphous or polycrystalline. On the other hand, the deposition rate is higher and thus the statistical character of the atomic deposition is more pronounced than in the MBE process. The structural parameters controlling the application of the respective multilayer films for x-ray optics, for example, are the waviness and roughness of the interfaces and the thickness of the individual sublayers. Depending on the growing mode, the initial long-range waviness and the interface roughness of the substrate may be either replicated layer-by-layer or smoothed out during the deposition process. The lateral and vertical correlation of these parameters is worthy of detailed investigation because the parameters provide insights into the growing process itself.

Organic layers were deposited by rather crude methods, such as spin-coating or Langmuir-Blodgett transfer from a liquid surface. The structure of these layers depends on whether self-organization takes place or not, so they can be deposited layer-by-layer often accompanied by reducing layer perfection. The in-plane structure of lipid layers, for example, behaves like a two-dimensional powder. During heating liquid crystals undergo several structural phase-transitions, changing the lateral and vertical ordering of molecules. Lipid layers can be combined with polymers or with layers containing inorganic species to supramolecular structures. Characterization of the three-dimensional structure is important for understanding the functionality of these supramolecular structures, which may differ from the individual

functions of the constituents. Considering the different size and ordering of molecules in lateral and vertical directions, different methods of structural investigation are required, i.e., x-ray reflectivity in the vertical, but x-ray diffraction in the lateral, direction.

Individual layers and interfaces within a layering heterostructure or a multilayer are identified rather indirectly. Due to the Fourier character of x-ray scattering, the particular layer or interface is measured as a scattering peak appearing at a certain scattering angle with definite intensity and definite peak shape. The peak shape, in particular, depends on the correlation length of structural attributes, i.e. the distance and number of structural features along the interface contributing to the scattering peak with equal phase. As in conventional optics the angular position and the peak width is inversely proportional to the number and distance of these scattering objects. This reciprocity is the reason for describing x-ray scattering in *reciprocal space* instead of direct space. However, in the best case, the correlation length of structural features equals that of the whole crystal. The corresponding peak shape can be entirely described by the dynamical theory of x-ray diffraction [270]. Any reduction of the correlation length, whether it is caused by the finite size of the crystal or by structural defects within a large crystal, reduces the correlation length and subsequently increases the peak width. These cases can be described in terms of the kinematic scattering theory as in Warren [386], for example. Although the basic theories are well known [175, 213, 270, 396], their application on thin layer and multilayer analysis requires a number of modifications and extensions of the theory, which demands a separate treatment.

For many problems x-ray scattering methods are complementary to scanning-probe techniques. Whereas scanning techniques, ergo atomic-force microscopy, provide a direct picture of a particular surface area, x-ray scattering gives a measure of the reciprocal space of the sample, which represents structural information averaged over a large sample volume. In addition, x-ray techniques are non-destructive and give access to internal interfaces, and they can be fast when using highly intense x-ray sources. Because the x-ray refraction index for matter is smaller than unity, x-ray methods can be depth selective if the beam strikes the sample surface under a shallow angle of incidence. Thus very thin layers and surface elevations of a few nanometers can be measured.

At present, x-ray techniques are routine methods in scientific material science laboratories and one can find more and more applications to routine probes of industrial processes. The wide use of x-ray diffraction techniques is based on new developments in x-ray scattering equipment. Nowadays x-ray tubes can provide an incident intensity which is comparable to that of a bending magnet at a synchrotron facility. Modern x-ray diffractometers and reflectometers are equipped with optimized optical elements which give the user flexibility in the choice of experimental conditions. Therefore these

instruments can be used for high-resolution experiments as well as for the measurement of imperfect materials.

This book is a second edition of our previous monograph, *High-Resolution X-Ray Scattering from Thin Films and Multilayers* [167], which appeared in 1999. Before this, there was no particular monograph in the literature dealing with the problem of x-ray diffractometry and reflectometry from thin films. At nearly the same time other books appeared describing one [8, 120, 376] or both topics [61]. Despite this competition our book experienced good acceptance by readers and was sold out after two years. This might have been caused by the general architecture of the book, which can be helpful for newcomers as well as experienced researchers.

Our book displays a synergetic structure of four main parts - *Experimental Realization, Basic Principles, Solution of Experimental Problems*, and *X-Ray Scattering by Laterally Structured Semiconductor Nanostructures* - presented in mutual connection to one another. Nevertheless, each part is organized in such a way that it can be understood separately to a large extent. The first part will introduce the reader to the general set-up of an x-ray reflection and x-ray diffraction experiment and in the function and arrangement of optical elements to achieve the experimental resolution *necessary* to solve a particular problem.

The second part describes the underlying theory in an extensive way; it describes all the formulas necessary to interpret an x-ray reflection or diffraction experiment and considers the kinematic and dynamical theories of x-ray diffraction which are used to simulate the scattering curves presented in the experimental chapters.

Finally, the third and fourth parts, which are the longest ones, present a lot of experimental problems, which have been solved by the authors and in other laboratories in the past. There are problems of the thickness determination of layers with thicknesses of less than 5 nm, the thickness determination of multilayer structures, the measurement of misfits and interface strains, the determination of the interface roughness, and correlation properties of the interface roughness and of crystal defects. As in the previous edition we focus our interest on actual problems of x-ray diffraction analysis and the investigation of lateral nanostructures, such as surface gratings and quantum dots. The examples presented were taken from scientific projects dealing with either semiconductors, metals, or organic materials. Thus we believe that the experience transmitted by us is of a general nature and not restricted to sophisticated problems. The third and fourth parts are self-explanatory but refer to expressions of general theory given in Part II.

All the chapters in the first edition were critically reviewed. Obvious misprints and errors were corrected and ambiguous phrases were reformulated. In the first part we considered new commercial instruments that appeared on the market during the last years, providing an increasing x-ray flux for home laboratory apparatus. Also the new challenge in the production of syn-

chrotron radiation, the free-electron laser, is addressed. The theoretic part is completed by the formalism of *Distorted-Wave Born Approximation*. This became necessary for the description of statistical properties of surfaces and interfaces and, in particular, of semiconductor quantum dot structures.

The examples of the third part also were revised. Many figures were replaced by actual examples taken in our laboratories and from laboratories of the Ferdinand-Braun Institut (Berlin); the universities of Würzburg, Linz, and Magdeburg, and the European Synchrotron Radiation Facility in Grenoble (ESRF), the Hamburger Synchrotron Strahlungslabor (HASYLAB), and the company Bruker AXS. The chapter about gratings and dots was rewritten and much extended. It is now divided into three chapters (12 - 14) because of the many new results received by the authors over the last years: Chapter 12, dealing with periodic surface nanostructures, is completed by examples of organic and metallic systems. Chapter 13 considers the problem of strain analysis in artificially structurized lateral nanostructures. The strain and correlation properties of quantum dot structures are described in chapter 14.

Finally, the authors thank several people who have helped us during the preparation of the manuscript. First of all, there are all our co-workers and Ph.D. students who have worked with us during the last years in our laboratories. In additon, besides many others, we thank Bernd Husemann for technical assistance while preparing the LATEX-style manuscript and Daniel Lübbert and Birgit-Marina Pietsch for support with the graphics design. Finally we thank the Bruker AXS GmbH, Karlsruhe for providing schemes of new technical solutions.

Potsdam, Germany — *Ullrich Pietsch*
Brno, Czech Republic — *Vaclav Holý*
Karlsruhe, Germany — *Tilo Baumbach*
February 2004

http://www.springer.com/978-0-387-40092-1

High-Resolution X-Ray Scattering
From Thin Films to Lateral Nanostructures
Pietsch, U.; Holy, V.; Baumbach, T.
2004, XVI, 408 p. 389 illus., Hardcover
ISBN: 978-0-387-40092-1