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## Introduction

Physics and chemistry of surfaces and interfaces is one of the most challenging areas of modern science, in view of its numerous applications in various fields of science and technology. Various technologically important processes occur either in the surface region of crystals or at the boundary between different media. For example, the fast development of microelectronics was promoted by a deepening of our understanding of electronic processes at interfaces between a semiconductor and a metal or another semiconductor. Heterogeneous catalysis is essentially chemistry at surfaces and thus demands a thorough knowledge of molecular processes at a gas–solid interface. Electrochemistry is based on similar processes that occur at an interface between a metal electrode and an electrolyte solution. Heat and mass transfer as well as the phenomenon of friction are determined by physical properties of an interface between contacting media as well as by elementary processes which occur on it. Such important modern techniques as molecular beam epitaxy and chemical vapor deposition are directly related to phenomena at solid surfaces. This list is far from being complete and can be continuously increased.

The main problem which an investigator faces in surface and interface science is that the number of atoms or molecules in the surface or interface region is small compared with those in the bulk. It is therefore necessary to have specific analytical tools at hand which are sensitive to surface and interface properties as well as to processes which occur in those regions. Among the different analytical techniques which have been developed in surface science over the years, optical techniques have definite advantages determined by their non-perturbing character, reliability and ease of use. They do not require ultrahigh vacuum and can be applied under good vacuum and ambient conditions as well, thus allowing one *in situ* investigations. To bring the whole into context we note that, in fact, this very branch of surface science dates back to 1890 when Drude studied the reflection of light from crystal surfaces in the presence of surface contamination. In this sense optical methods were the first to allow truly surface-specific investigations.

This book begins with an introductory chapter to surface and interface science. Different properties of crystal surfaces and their interfaces to liquids and gases are considered. The next chapter is devoted to linear optical properties of surfaces as well as of interfaces between two media. Although the contacting media are described in terms of their dielectric functions, the relevant theory is equally valid for solids, liquids and gases, except some explicitly specified cases. Analytical techniques considered in this book can be broadly classified as infrared and optical where the term *optical* implies the use of electromagnetic radiation in the visible spectral range or close to it. With the invention of lasers operating in different spectral regimes, the possibilities of optical analytical techniques have been extended considerably. Both linear and nonlinear laser spectroscopy is widely used nowadays in surface and interface analysis and thus is discussed with some broadness in this book. Lasers provide high brightness, monochromaticity and directivity of the probing light. Ultrashort pulsed lasers allow one to monitor temporal behavior of surface processes with unprecedented precision.

An interface between two media is accessible for light if at least one of the media is transparent in the considered spectral region. Therefore, optical tools can be exploited for interface analysis in the ranges of transparency of the contacting media. However, the range of applicability of optical techniques can be significantly extended if the incident light excites electromagnetic modes bound to the interface. Such electromagnetic waves are called surface polaritons. For example, at a metal surface they can be excited in a wide spectral range from the far infrared to the far ultraviolet region. The use of surface polaritons for surface and interface analysis is therefore discussed at various places in this book.

A measurement of the reflection coefficient of light is the most simple and oldest optical technique, providing information on a surface or an interface. Being applied to an interface between a solid and a gaseous phase it reflects the features of the gas optical spectrum. However, it was only discovered during the fifties of the last century, that at relatively low gas pressures the reflection of light resonant to the transition in gas atoms in such a system displays peculiarities which can be attributed to gas–surface scattering. This relatively new field of optical spectroscopy has received growing attention recently, prompting us to discuss it in some more detail.

A traditional branch of surface optics is optical microscopy, i.e., imaging of objects disposed on a surface. Since the invention of the first optical microscopes in the 16<sup>th</sup> century this field has undergone strong and permanent progress. In addition to bright-field, microscopy images can also be obtained by dark and near-field microscopy, resulting in large contrast improvement and better and better resolution. Sophisticated implementation of laser scanning techniques has led to what one usually calls ultramicroscopy. Easy ac-

cess to three-dimensional images becomes possible via confocal approaches. Finally, the use of nonlinear optical and polarization techniques gives access even to buried interfaces.

We conclude the book with a discussion of optical tools with high spatial resolution that match recent demands from nanoscience and nanotechnology. This new class of optical devices, such as scanning near-field optical microscopes or photon scanning tunneling microscopes, has been developed to investigate surface properties at the nanometer scale. The same tools are capable of registering optical spectra locally, reaching the limit of single molecule spectroscopy.

This book is a textbook and as such it can be used in a consecutive way for lecturing chapter by chapter. However, we have tried to make each chapter also understandable in itself, considerably restricting the number of cross references. Throughout the text, references to specific literature are given. The interested reader can find more general literature on the topics of the individual chapters at the end in a Further Reading section.

Some of the theoretical formulation is not very straightforward. Therefore, we have printed the text in small letters which can be skipped at a first short reading. We suggest working through the problems that are given at the end of the chapters which should serve to strengthen the readers capability of handling problems of optics at surfaces. Solutions are added at the very end of the book.

Finally, in order to avoid multiple definitions of the same terms we have added a brief glossary and also an index that allows one to look up specific topics.

