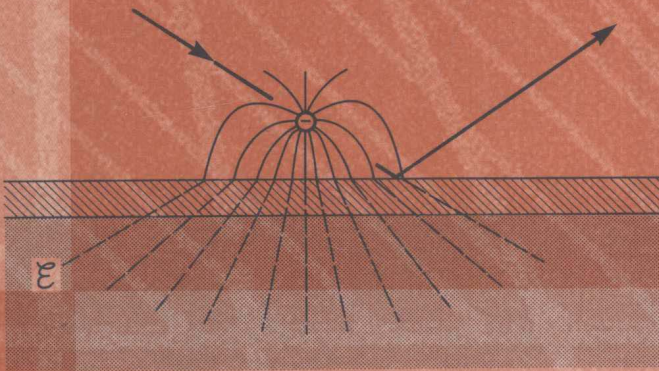


H. Lüth

Solid Surfaces, Interfaces and Thin Films

Fourth Edition

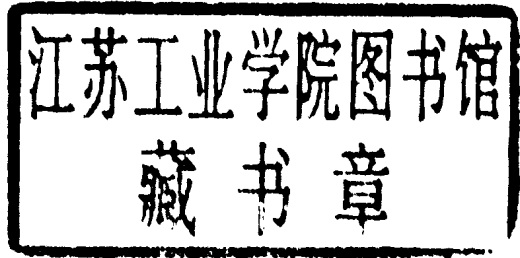


Springer

Hans Lüth

Solid Surfaces, Interfaces and Thin Films

Fourth, Revised and Extended Edition
With 389 Figures and 13 Tables



Springer

Professor Dr. Hans Lüth
Forschungszentrum Jülich GmbH
Institut für Schichten und Grenzflächen
52425 Jülich
and
Rheinisch-Westfälische Technische Hochschule
52062 Aachen
Germany
E-mail: h.lueth@fz-juelich.de

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Preface

Surface physics in the classical sense of ultrahigh vacuum (UHV) based experimental approaches to understand well-defined surfaces has now become a mature branch of condensed matter research. Meanwhile, however, the theoretical concepts and experimental techniques developed in this field have also become the basis for modern interface, thin film and nanostructure science. Furthermore, these research fields are of fundamental importance for more applied branches of science, such as micro- and nanoelectronics, catalysis and corrosion research, surface protection, chemo- and biosensors, microsystems and nanostructured materials.

The physics of solid surfaces, interfaces and thin films is thus an important field which needs to be taught to all students in physics, microelectronics, engineering and material science. It is thus no surprise that this topic has now entered the corresponding university curricula throughout the world.

In the present 4th edition of this book (formerly entitled “Surfaces and Interfaces of Solid Materials”) more emphasis is placed on the relation between the surfaces, interfaces and thin films, and on newly discovered phenomena related to low dimensions. Accordingly, a few topics of the earlier editions that are now only of peripheral interest have been omitted. On the other hand, a new chapter dealing with collective phenomena at interfaces has been added: Superconductor- semiconductor interfaces and thin ferromagnetic films have attracted considerable attention in of late. This is mainly due to our improved understanding of these phenomena, but also to important application aspects which have recently emerged. For example, giant magnetoresistance, a typical thin film phenomenon, is of considerable importance for read-out devices in magnetic information storage. Likewise, ferromagnetism in low dimensions may play an important role in future non-volatile memory device circuits. The corresponding topics have thus been added to the new edition and the title of the book has been modified slightly to “Solid Surfaces, Interfaces and Thin Films”. This new title better describes the wider range of topics treated in the new edition.

Furthermore, in response to several suggestions from students and colleagues, errors and inconsistencies in the text have been eliminated and improvements made to clarity. On the topics superconductor–semiconductor interfaces and ferromagnetism in low dimensions, I have benefited from dis-

cussions with Thomas Schäpers and Stefan Blügel, respectively. The English text was significantly improved by Angela Lahee, who, together with Katharina Ascheron, also contributed much to the final production of the book.

Particular thanks are due to Claus Ascheron of Springer-Verlag, who managed the whole publication process.

Aachen and Jülich
July 2001

Hans Lüth

Preface to the Second Edition

Surface and interface physics has in recent decades become an ever more important subdiscipline within the physics of condensed matter. Many phenomena and experimental techniques, for example the quantum Hall effect and photoemission spectroscopy for investigating electronic band structures, which clearly belong to the general field of solid-state physics, cannot be treated without a profound knowledge of surface and interface effects. This is also true in view of the present general development in solid-state research, where the quantum physics of nanostructures is becoming increasingly relevant. This also holds for more applied fields such as microelectronics, catalysis and corrosion research. The more one strives to obtain an atomic-scale understanding, and the greater the interest in microstructures, the more surface and interface physics becomes an essential prerequisite.

In spite of this situation, there are only a very few books on the market which treat the subject in a comprehensive way, even though surface and interface physics has now been taught for a number of years at many universities around the world. In my own teaching and research activities I always have the same experience: when new students start their diploma or PhD work in my group I can recommend to them a number of good review articles or advanced monographs, but a real introductory and comprehensive textbook to usher them into this fascinating field of modern research has been lacking.

I therefore wrote this book for my students to provide them with a text from which they can learn the basic models, together with fundamental experimental techniques and the relationship to applied fields such as microanalysis, catalysis and microelectronics.

This textbook on the physics of surfaces and interfaces covers both experimental and theoretical aspects of the subject. Particular attention is paid to practical considerations in a series of self-contained panels which describe UHV technology, electron optics, surface spectroscopy and electrical and optical interface characterisation techniques. The main text provides a clear and comprehensive description of surface and interface preparation methods, structural, vibrational and electronic properties, and adsorption and layer growth. Because of their essential role in modern microelectronics, special emphasis is placed on the electronic properties of semiconductor interfaces

and heterostructures. Emphasizing semiconductor microelectronics as one of the major applications of interface physics is furthermore justified by the fact that here the gap between application and basic research is small, in contrast, for example, with catalysis or corrosion and surface-protection research.

The book is based on lectures given at the Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen and on student seminars organized with my colleagues Pieter Balk, Hans Bonzel, Harald Ibach, Jürgen Kirchner, Claus-Dieter Kohl and Bruno Lengeler. I am grateful to these colleagues and to a number of students participating in these seminars for their contributions and for the nice atmosphere during these courses. Other valuable suggestions were made by some of my former doctoral students, in particular by Arno Förster, Monika Mattern-Klosson, Richard Matz, Bernd Schäfer, Thomas Schäpers, Andreas Spitzer and Andreas Tulke. For her critical reading of the manuscript, as well as for many valuable contributions, I want to thank Angela Rizzi.

The English text was significantly improved by Angela Lahec from Springer Verlag. For this help, and also for some scientific hints, I would like to thank her. For the pleasant collaboration during the final production of the book I thank Ilona Kaiser. The book would not have been finished without the permanent support of Helmut Lotsch; many thanks to him as well.

Last, but not least, I want to thank my family who missed me frequently, but nevertheless supported me patiently and continuously during the time in which I wrote the book.

Aachen and Jülich
October 1992

Hans Lüth

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1. Surface and Interface Physics: Its Definition and Importance

A solid interface is defined as a small number of atomic layers that separate two solids in intimate contact with one another, where the properties differ significantly from those of the bulk material it separates. A metal film deposited on a semiconductor crystal, for example, is thus separated by the semiconductor-metal interface from the bulk of the semiconductor.

The surface of a solid is a particularly simple type of interface, at which the solid is in contact with the surrounding world, i.e., the atmosphere or, in the ideal case, the vacuum. The development of modern interface and thin film physics is thus basically determined by the theoretical concepts and the experimental tools being developed in the field of surface physics, i.e., the physics of the simple solid-vacuum interface. Surface physics itself has meanwhile become an important branch of microscopic solid-state physics, even though its historical roots lie both in classical bulk solid-state physics and physical chemistry, in particular the study of surface reactions and heterogeneous catalysis.

Solid-state physics is conceptually an atomic physics of the condensed state of matter. According to the strength of chemical bonding, the relevant energy scale is that between zero and a couple of electron volts. The main goal consists of deriving an atomistic description of the macroscopic properties of a solid, such as elasticity, specific heat, electrical conductance, optical response or magnetism. The characteristic difference from atomic physics stems from the necessity to describe a vast number of atoms, an assembly of about 10^{23} atoms being contained in 1 cm^3 of condensed matter; or the 10^8 atoms that lie along a line of 1 cm in a solid. In order to make such a large number of atoms accessible to a theoretical description, new concepts had to be developed in bulk solid-state physics. The translational symmetry of an ideal crystalline solid leads to the existence of phonon dispersion branches or the electronic band structure and the effective mass of an electron. Because of the large number of atoms involved, and because of the difference between the macroscopic and the atomic length scale, most theoretical models in classic solid-state theory are based on the assumption of an infinitely extended solid. Thus, in these models, the properties of the relatively small number of atoms forming the surface of the macroscopic solid are neglected. This simplifies the mathematical description considerably. The infinite translational

symmetry of the idealized crystalline solid allows the application of a number of symmetry operations, which makes a handy mathematical treatment possible. This description of the solid in terms of an infinitely extended object, which neglects the properties of the few different atomic layers at the surface, is a good approximation for deriving macroscopic properties that depend on the total number of atoms contained in this solid. Furthermore, this description holds for all kinds of spectroscopic experiments, where the probes (X-rays, neutrons, fast electrons, etc.) penetrate deep into the solid material and where the effect of the relatively few surface atoms ($\approx 10^{15} \text{ cm}^{-2}$) can be neglected.

The approach of classical solid-state physics in terms of an infinitely extended solid becomes highly questionable and incorrect, however, when probes are used which “strongly” interact with solid matter and thus penetrate only a couple of Ångströms into the solid, such as low-energy electrons, atomic and molecular beams, etc. Here the properties of surface atoms, being different from those of bulk atoms, become important. The same is true for spectroscopies where the particles detected outside the surface originate from excitation processes close to the surface. In photoemission experiments, for example, electrons from occupied electronic states in the solid are excited by X-rays or UV light; they escape into the vacuum through the surface and are analysed and detected by an electron spectrometer. Due to the very limited penetration depth of these photoelectrons (5-80 Å depending on their energy) the effect of the topmost atomic layers below the surface cannot be neglected. The photoelectron spectra carry information specific to these topmost atomic layers. Characteristic properties of the surface enter the theoretical description of a photoemission experiment (Panel XI: Chap. 6). Even when bulk electronic states are studied, the analysis of the data is done within the framework of models developed in surface physics. Furthermore, in order to get information about intrinsic properties of the particular solid, the experiment has to be performed under Ultra-High Vacuum (UHV) conditions on a freshly prepared clean sample surface. Because of the surface sensitivity, the slightest contamination on the surface would modify the results.

The concepts of surface and interface physics are important in solid-state physics not only in connection with special experimental tools, but also for certain physical systems. A thin solid film deposited on a substrate is bounded by a solid–solid interface and by its surface (film vacuum interface). The properties of such a thin film are thus basically determined by the properties of its two interfaces. Thin-film physics cannot be reduced to the concepts of bulk solid-state physics, but instead the models of interface physics have to be applied. Similarly, the physics of small atomic clusters, which often possess more surface than “bulk” atoms, must take into account the results from surface physics.

Surface and interface physics, as a well-defined sub-discipline of general condensed-matter physics, is thus interrelated in a complex way with a num-

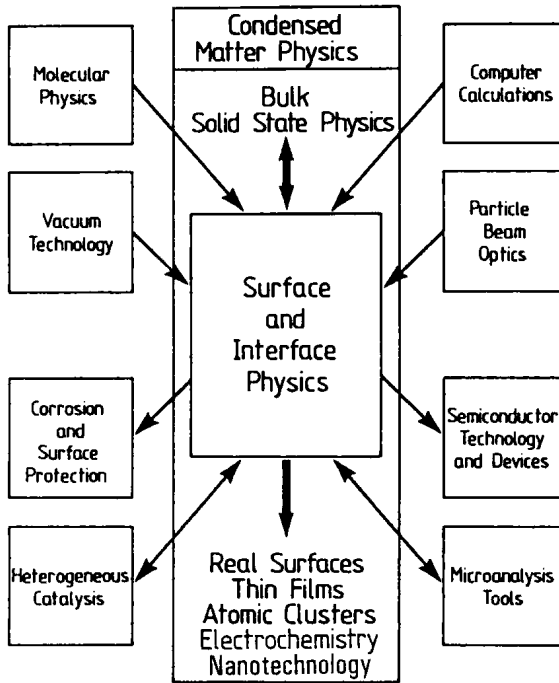


Fig. 1.1. Interrelation of surface and interface physics as a subdiscipline of condensed-matter physics with other research fields

ber of other research fields (Fig. 1.1). This is particularly true if one considers the input from other domains of physics and chemistry and the output into important fields of application such as semiconductor electronics and the development of new experimental equipment and methods. The scheme in Fig. 1.1 emphasises the way in which surface and interface physics is embedded in the general field of condensed-matter physics, as well as the strong impact of the models of bulk solid-state physics (phonon dispersion, electronic bands, transport mechanisms, etc.) on the concepts of interface physics.

On the other hand, within general solid-state physics, interface physics provides a deeper understanding of the particular problems related to the real surfaces of a solid and to thin films, dealing with both their physical properties and their growth mechanisms. The physics of small atomic clusters also benefits from surface physics, as does the wide field of electro-chemistry, where the reaction of solid surfaces with an ambient electrolyte is the central topic. Furthermore, the new branch of nanotechnology, i.e. engineering on a nanometer scale (Panel VI: Chap. 3), which has emerged as a consequence of the application of scanning tunneling microscopy and related techniques, uses concepts that have largely been developed in surface sciences.

Modern surface and interface physics would not have been possible without the use of results from research fields other than bulk solid-state physics. From the experimental viewpoint, the preparation of well-defined, clean surfaces, on which surface studies are usually performed, became possible only after the development of UHV techniques. Vacuum physics and technology had a strong impact on surface and thin film physics. Surface sensitive spectroscopies use particles (low-energy electrons, atoms, molecules, etc.) because of their "strong" interaction with matter, and thus the development of particle beam optics, spectrometers and detectors is intimately related to the advent of modern surface physics. Since adsorption processes on solid surfaces are a central topic in surface physics, not only the properties of the solid substrate but also the physics of the adsorbing molecule is an ingredient in the understanding of the complex adsorption process. The physics and chemistry of molecules also plays an essential role in many questions in surface physics. Last, but not least, modern surface and interface physics would never have reached the present level of theoretical understanding without the possibility of large and complex computer calculations. Many calculations are much more extensive and tedious than in classical bulk solid-state physics since, even for a crystalline solid, a surface or interface breaks the translational symmetry and thus considerably increases the number of equations to be treated (loss of symmetry).

From the viewpoint of applications, surface and interface physics can be considered as the basic science for a number of engineering branches and advanced technologic. A better understanding of corrosion processes, and thus also the development of surface protection methods, can only be expected on the basis of surface studies. Modern semiconductor device technology would be quite unthinkable without research on semiconductor surfaces and interfaces. With an increasing trend towards greater miniaturization (large-scale integration) surfaces and interfaces become an increasingly important factor in the functioning of a device. Furthermore, the preparation techniques for complex multilayer device structures - Molecular Beam Epitaxy (MBE), metal organic MBE (Chap. 2) - are largely derived from surface-science techniques. In this field, surface science research has led to the development of new technologies for semiconductor-layer preparation.

An interdependence between surface physics and applied catalysis research can also be observed. Surface science has contributed much to a deeper atomistic understanding of important adsorption and reaction mechanisms of molecules on catalytically active surfaces, even though practical heterogeneous catalysis occurs under temperature and pressure conditions totally different from those on a clean solid surface in a UHV vessel. On the other hand, the large amount of knowledge derived from classical catalysis studies under less well-defined conditions has also influenced surface science research on well-defined model systems. A similar interdependence exists between surface physics and the general field of applied microanalysis. The de-

mand for extremely surface-sensitive probes in surface and interface physics has had an enormous impact on the development and improvement of new particle spectroscopies. Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectroscopy (SIMS) and High-Resolution Electron Energy Loss Spectroscopy (HREELS) are good examples. These techniques were developed within the field of surface and interface physics [1.1]. Meanwhile they have become standard techniques in many other fields of practical research, where microanalysis is required.

Surface and interface physics thus has an enormous impact on other fields of research and technology. Together with the wide variety of experimental techniques being used in this field, and with the input from various other branches of chemistry and physics, it is a truly interdisciplinary field of physical research.

Characteristic for this branch of physics is the intimate relation between experimental and theoretical research, and the application of a wide variety of differing experimental techniques having their origin sometimes in completely different fields. Correspondingly, this text follows a concept, where the general theoretical framework of surface and interface physics, as it appears at present, is treated in parallel with the major experimental methods described in so-called panels. In spite of the diversity of the experimental methods and approaches applied so far in this field, there is one basic technique which seems to be common to all modern surface, interface and thin film experiments: UHV equipment is required to establish clean conditions for the preparation of a well-defined solid surface or the performance of in situ studies on a freshly prepared interface. If one enters a laboratory for surface or interface studies, large UHV vessels with corresponding pumping stations are always to be found. Similarly, the importance of particle-beam optics and analytical tools, in particular for low-energy electrons, derives from the necessity to have surface sensitive probes available to establish the crystallographic perfection and cleanliness of a freshly prepared surface.