PHY

国外物理名著系列 2

（影印版）

# Principles of Surface Physics

# 表面物理原理

F. Bechstedt

科学出版社
www.sciencep.com

**图字:01-2007-1093**

**图书在版编目(CIP)数据**

表面物理原理=Principles of Surface Physics:英文/(德)贝希施泰特(Bechstedt,F.)编著.—影印本.—北京:科学出版社,2007

(国外物理名著系列;2)

ISBN 978-7-03-018788-8

Ⅰ.表… Ⅱ.贝… Ⅲ.表面物理学-英文 Ⅳ.O485

中国版本图书馆 CIP 数据核字(2007)第 042390 号

责任编辑:胡凯 鄢德平/责任印制:赵德静/封面设计:陈敬

科学出版社 出版
北京东黄城根北街16号
邮政编码:100717
http://www.sciencep.com
中国科学院印刷厂 印刷
科学出版社发行 各地新华书店经销
*
2007年4月第 一 版 开本:B5(720×1000)
2007年4月第一次印刷 印张:22 1/2
印数:1—3 000 字数:420 000

**定价:58.00 元**

(如有印装质量问题,我社负责调换〈科印〉)

# 《国外物理名著系列》(影印版)专家委员会名单

（按姓氏笔画排序）

# 国外物理名著(影印版)系列序言

对于国内的物理学工作者和青年学生来讲，研读国外优秀的物理学著作是系统掌握物理学知识的一个重要手段。但是，在国内并不能及时、方便地买到国外的图书，且国外图书不菲的价格往往令国内的读者却步，因此，把国外的优秀物理原著引进到国内，让国内的读者能够方便地以较低的价格购买是一项意义深远的工作，将有助于国内物理学工作者和青年学生掌握国际物理学的前沿知识，进而推动我国物理学科研和教学的发展。

为了满足国内读者对国外优秀物理学著作的需求，科学出版社启动了引进国外优秀著作的工作，出版社的这一举措得到了国内物理学界的积极响应和支持，很快成立了专家委员会，开展了选题的推荐和筛选工作，在出版社初选的书单基础上确定了第一批引进的项目，这些图书几乎涉及了近代物理学的所有领域，既有阐述学科基本理论的经典名著，也有反映某一学科专题前沿的专著。在选择图书时，专家委员会遵循了以下原则：基础理论方面的图书强调“经典”，选择了那些经得起时间检验、对物理学的发展产生重要影响、现在还不“过时”的著作（如：狄拉克的《量子力学原理》）。反映物理学某一领域进展的著作强调“前沿”和“热点”，根据国内物理学研究发展的实际情况，选择了能够体现相关学科最新进展，对有关方向的科研人员和研究生有重要参考价值的图书。这些图书都是最新版的，多数图书都是2000年以后出版的，还有相当一部分是2006年出版的新书。因此，这套丛书具有权威性、前瞻性和应用性强的特点。由于国外出版社的要求，科学出版社对部分图书进行了少量的翻译和注释（主要是目录标题和练习题），但这并不会影响图书“原汁原味”的感觉，可能还会方便国内读者的阅读和理解。

“他山之石，可以攻玉”，希望这套丛书的出版能够为国内物理学工作者和青年学生的工作和学习提供参考，也希望国内更多专家参与到这一工作中来，推荐更多的好书。

杨国桢

中国科学院院士

中国物理学会理事长

2007年3月20日

To Andreas, Susanne, and Uta

All the rivers run into the sea; yet the sea is not full; unto the place from whence the rivers come, thither they return again.

All things are full of labour; man cannot utter it: the eye is not satisfied with seeing, nor the ear filled with hearing.

Ecclesiastes
(or, The Preacher)

# Preface

In recent decades, surface and interface physics has become an increasingly important subdiscipline within the physics of condensed matter as well as an interdisciplinary field between physics, crystallography, chemistry, biology, and materials science. There are several driving forces for the development of the field, among them semiconductor technology, new materials, epitaxy and chemical catalysis. The electrical and optical properties of nanostructures based on different semiconductors are governed by the interfaces or, at least, by the presence of interfaces. A microscopic understanding of the growth processes requires the investigation of the surface processes at an atomic level. Elementary processes on surfaces, such as adsorption and desorption, play a key role in the understanding of heterogeneous catalysis.

During the course of the surface investigations, it has been possible to observe a dramatic progress in the ability to study surfaces of materials in general, and on a microscopic scale in particular. There are two main reasons for this progress. From the experimental point of view it is largely due to the development and availability of new types of powerful microscopes. Spectacular advances in techniques such as scanning tunneling microscopy now allow us to observe individual atoms on surfaces, and to follow their paths with a clarity unimaginable a few years ago. From the theoretical point of view (or rather the viewpoint of simulation) progress is related to the wide availability of computers and the dramatic increase of their power. Today, early methodological developments such as density functional theory allow a full quantum-mechanical treatment of electrons in materials. In the future, computer experiments will be able to simulate the behavior of surfaces and processes on surfaces at the level of individual atomic cores and their surrounding electrons with high accuracy and remarkable predictive power.

This enormous progress in surface science has been documented in many excellent books on surface structures, surface processes, theoretical modeling of surfaces, and surfaces and interfaces of particular solids like semiconductors. However, only very few books try to treat the subject in a unified and comprehensive way. This holds true in particular for the experimental and theoretical methods used in surface physics and, most of all, for the principles and concepts. Hence I perceived the need for a book dealing with surface physics at the level of an advanced textbook. The aim here is to describe the fundamentals of the field and to provide a framework for the discussion of surface phenomena in a single text. Examples of particular surfaces of materials such as semiconductors or metals are only discussed as a means of illustrating the fundamentals or principles. Special theoretical or experimental methods of surface studies are mentioned but not described in detail. Particular attention is paid to physical approaches that can be applied to the discovery and discussion of novel surface phenomena. Among them are symmetry arguments, energetics, driving forces and elements of geometrical changes, elementary excitations, and other characteristic properties. These elements should help to classify surface problems and to facilitate their understanding. The only prior knowledge assumed is undergraduate physics and mathematics course material. Mainly textbook quantum mechanics and geometrical arguments are used to discuss and describe surfaces and surface processes. Graduate-level topics such as second quantization are avoided. Whenever many-body arguments are needed, a brief (more phenomenological) introduction is given. Green's functions are introduced by using their relationship to observable quantities. The use of group theory is restricted to geometrical arguments and its notations. Feynman diagrams are only shown to illustrate interactions between particles on surfaces. An extended subject index will help students and scientists to use the book for reference and during their every-day scientific work. To keep formulas to a manageable length, they are written in the framework of cgs units. In addition, use is made of the fact that the energies of valence electrons are of the order of electron volts and atomic distances are of the order of angstroms.

The book is based on lectures given at the Humboldt-Universität zu Berlin and the Friedrich-Schiller-Universität Jena and on student seminars. I would like to acknowledge many discussions with colleagues around the world. I also thank my colleagues and students for their critical reading of parts of the manuscript. Among others I am indebted to R. Del Sole, N. Esser, J. Furthmüller, S. Glutsch, P. Kratzer, J. Neugebauer, G. Onida, M. Rohlfing, A. Schindlmayr, W.G. Schmidt, and J.-M. Wagner. The typing of the manuscript was achieved with competence and infinite patience by my secretary Sylvia Hofmann. Coordination and production of the book were undertaken by Petra Treiber and Angela Lahee from Springer Verlag.

Jena, March 2003 *Friedhelm Bechstedt*

# Contents

# 1. Symmetry

## 1.1 Model Surfaces

### 1.1.1 Surface Versus Bulk

Every real solid is bounded by surfaces. Nonetheless, the model of an infinite solid which neglects the presence of surfaces works very well in the case of many physical properties. The reason is, firstly, that one usually deals with properties, such as transport, optical, magnetic, mechanical or thermal properties, to which all the atoms of the solid contribute more or less to the same extent, and, secondly, that there are many more atoms in the bulk of a solid sample than at its surface, provided the solid is of macroscopic size. In the case of a silicon cube of 1 $\mathrm{cm}^3$, for example, one has $5 \times 10^{22}$ bulk atoms and $4 \times 10^{15}$ surface atoms.

The surface atoms are only visible in surface sensitive experimental techniques or by studying properties or processes which are determined by surface atoms only. Among them are phenomena like crystal growth, adsorption, oxidation, etching or catalysis. They cannot be described by the model of an infinite solid. However, there are also effects which are determined by the interplay of bulk and surface (or, more strictly speaking, the interface). For instance, the channel of the carrier transport in field-effect transistors is determined by the surface (interface) states as well as the bulk doping. In one of the first theoretical approaches to the field effect, Bardeen [1.1] applied the premise of charge neutrality at the surfaces/interfaces. This condition means that in thermal equilibrium the surface band bending adjusts in such a way that the net charge in surface states is balanced by a space charge below the surface of the semiconductor forming the main part of the electrical device.

### 1.1.2 The Surface as a Physical Object

Under normal conditions, i.e., atmospheric pressure and room temperature, the real surface of a solid is far removed from the ideal systems desirable in physical investigations. A freshly prepared surface of a material is normally very reactive toward atoms and molecules in the environment. All kinds of particle adsorption – from strong chemisorption to weak physisorption – give rise to an adlayer on the topmost atomic layers of the solid. One example is the immediate formation of an extremely thin oxide layer on a freshly cleaved silicon crystal. Usually the chemical composition and the geometrical structure of such a contamination adlayer are not well defined.

As an object of physical investigations a well-defined surface has to be prepared on a particular solid, in a special preparation process, under well-defined external conditions. Such a solid could be a crystalline material, a single crystal or a crystalline film deposited by epitaxy in a well-controlled way. A rather clean surface of such a crystalline system might also be prepared as an electrode surface in an electrochemical cell, or a semiconductor surface in a reactor where vapor phase epitaxy (VPE) is performed at standard pressure conditions and at elevated temperature. However, the processes of the underlying methods and the results are rather complex and difficult to characterize. The simplest ways to prepare a solid surface should happen in ultrahigh vacuum (UHV), i.e., at ambient pressure lower than $10^{-8}$ Pa (about $10^{-10}$ torr). There are essentially three ways to manufacture clean surfaces under UHV conditions:

i. Cleavage of brittle materials in UHV. Of course, only surfaces which are cleavage planes of the crystal can be made in this way.
ii. Treatment of imperfect and contaminated surfaces of arbitrary orientation by ion bombardment and thermal annealing (IBA), generally in several cycles. There are no limitations to certain materials and to certain crystallographic orientations.
iii. Epitaxial growth of crystal layers (or overlayers) by means of evaporation or molecular beam epitaxy (MBE).

Obviously, a smooth and clean surface cannot be realized in the ideal form, but rather only to some approximation. Any real surface will exhibit irregular deviations from perfect smoothness and purity despite the care taken in its preparation. An illustration of such a surface is given in Fig. 1.1. In reality a surface consists of a number of irregular portions of parallel surface lattice planes which are displaced vertically by one or more lattice plane separations with respect to each other. Atomic steps occur at the bound-

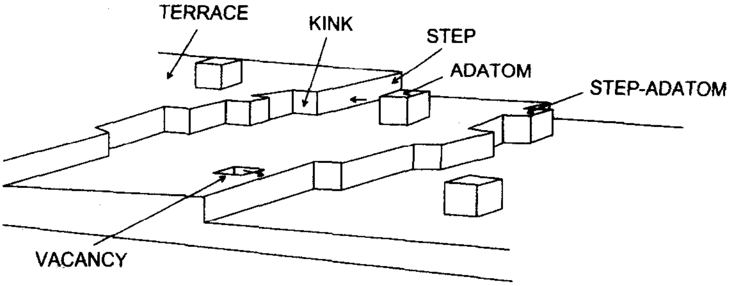

**Fig. 1.1.** Illustration of structural imperfections of crystal surfaces. Atoms and their electron shells are indicated by little cubes.

aries of these lattice-plane portions which in this context are called terraces. The steps may exhibit kinks. In addition to terraces, steps and kinks, other structural irregularities may occur which can be subsumed under the term 'surface roughness'. Adatoms and vacancies belong to this category, as do complexes of these simple defects. In the case of surfaces of compound crystals quite often atoms of one of the contributing elements are depleted more than those of the other which results in an enrichment of the latter and in a non-stoichiometry at the surface. The most significant form of chemical disturbance of surfaces, which applies both to compound and elemental crystals, is the contamination by impurities or adatoms of another species. The impurity atoms or adatoms may be situated at regular or nonregular sites of the surface lattice plane, at locations above and slightly below it.

## 1.2 Two-Dimensional Crystals

A complete characterization of a solid surface requires knowledge of not only atoms of 'what species' are present but 'where' they are. Just as in the bulk, it is not that the atomic coordinates as such are of much direct interest. Rather, besides the chemical nature of the atoms their geometrical arrangement governs the electronic, magnetic, optical, and other properties of surfaces.

### 1.2.1 Lattice Planes of Bulk Crystals

A geometrical construction which is of particular significance in describing crystal surfaces is that of a *lattice plane*. Lattice planes are usually denoted by *Miller indices* ($hkl$) where $h$, $k$, $l$ are the integer reciprocal axis intervals given by the intersections of the lattice planes with the three crystallographic axes. They have a simple meaning in the case of rectangular crystal systems, e.g., the cubic system. The symbol (100), for example, denotes lattice planes perpendicular to the cubic $x$-axis, (111) means lattice planes perpendicular to the body diagonal in the first octant of the cubic unit cell, and (110) denotes the lattice planes perpendicular to the face diagonal in the first quadrant of the $xy$-plane of the cubic unit cell. Usually, the collection of such planes that are equivalent by symmetry is labeled $\{hkl\}$. Thus {100} stands for the collection (100), ($\bar{1}00$), (010), ($0\bar{1}0$), (001) and ($00\bar{1}$), if these planes are equivalent. The bar notation $\bar{1}$ indicates the corresponding negative coefficient. In the case of trigonal and hexagonal lattices, four crystallographic axes are considered, three instead of two perpendicular to the $c$-axis. The lattice planes are then characterized by four indices ($hkil$) instead of three. The first three, however, are not independent of each other. In fact $h + k + i = 0$. The fourth axis (corresponding to the index $l$) is perpendicular to the hexagonal basal plane. The ($hkil$) are sometimes termed *Bravais indices.*

A particular geometrical plane can also be characterized by its normal direction

$$\boldsymbol{n} = \tilde{\boldsymbol{n}}/|\tilde{\boldsymbol{n}}|.$$

In the case of lattice planes it is convenient to relate it to a linear combination

$$\tilde{\boldsymbol{n}} = \frac{1}{2\pi}\left[h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3\right] \tag{1.1}$$

of the primitive vectors $\boldsymbol{b}_j$ $(j = 1, 2, 3)$ of the reciprocal lattice with the integer coefficients $h$, $k$, and $l$. The vectors $\boldsymbol{b}_j$ are directly related to the primitive lattice vectors $\boldsymbol{a}_i$ $(i = 1, 2, 3)$ by the relation

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = 2\pi\delta_{ij}. \tag{1.2}$$

Apart from the case of primitive Bravais lattices, they are different from the crystallographic axes. Anyway, a lattice plane can be characterized by the Miller indices $(hkl)$ and, hence, a normal parallel to the vector $\boldsymbol{G}_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$ of the reciprocal lattice. However, as a consequence of relation (1.2) the Miller indices depend on the particular choice of the primitive vectors of the Bravais lattice.

Miller indices are simplest to work with in simple cubic (sc) Bravais lattices, since the reciprocal lattice is also simple cubic and the Miller indices are the coordinates of a vector normal to the plane in the obvious Cartesian coordinate system. As a general rule, face-centered cubic (fcc) and body-centered cubic (bcc) Bravais lattices are described in terms of conventional cubic cells, i.e., as sc lattices with bases. Since any lattice plane in a bcc or fcc lattice is also a lattice plane in the underlying sc lattice, the same elementary cubic indexing $(hkl)$ can be used to specify lattice planes. This agreement simplifies a variety of considerations for a lot of materials. Many important metals consisting only of one element crystallize within the cubic crystal system. Also many elemental and compound semiconductors or strongly ionic compounds form diamond, zinc-blende, or rocksalt crystals which also belong to the cubic crystal system.

The Miller indices of a plane have a geometrical interpretation in real space. Therefore, a similar convention is used to specify directions in the direct lattice, but to avoid confusion with the Miller indices (directions in the reciprocal lattice) square brackets are used instead of parentheses. For instance, the body diagonal of a sc cubic lattice lies in the [111] direction and, in general, the lattice point $h\boldsymbol{a}_1 + k\boldsymbol{a}_2 + l\boldsymbol{a}_3$ lies in the direction $[hkl]$ from the origin. In the cubic case $[hkl]$ defines the normal direction of the plane $(hkl)$. The collection of such directions that are equivalent by symmetry is labeled $\langle hkl \rangle$. This holds in principle also for non-cubic Bravais lattices. However, in general the direction $[hkl]$ is not perpendicular to the plane $(hkl)$.

The property of the vector $\boldsymbol{G}_{hkl} = h\boldsymbol{b}_1 + k\boldsymbol{b}_2 + l\boldsymbol{b}_3$ of the reciprocal lattice can be proven characterizing the lattice planes by all possible Bravais lattice points

$$\boldsymbol{R}_l = \sum_{i=1}^{3} n_{li}\boldsymbol{a}_i \tag{1.3}$$

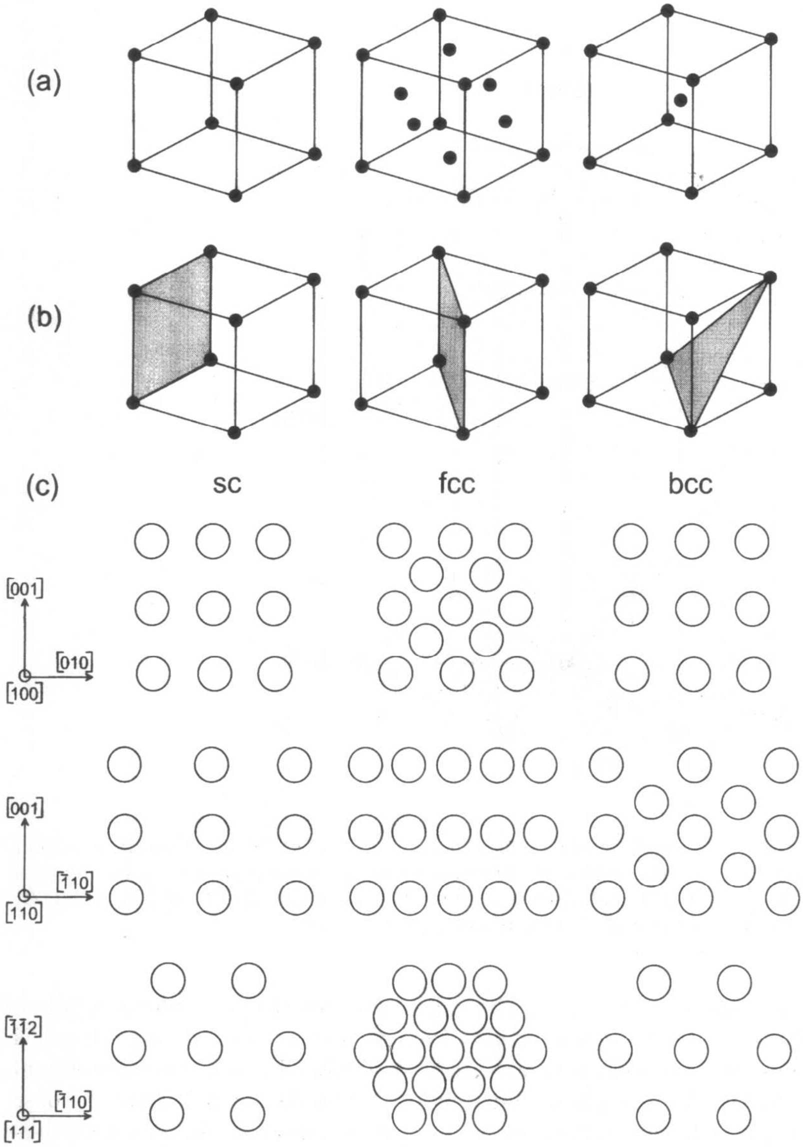

**Fig. 1.2.** (a) Cubic Bravais lattices sc, fcc, bcc; (b) low-index planes (100), (110), (111) in a sc cell; and (c) low-index planes resulting from cubic lattices. Bravais lattice points are indicated as dots (a,b) or spheres (c).