SURFACE PHYSICS OF MATERIALS

Volume 1

Edited by

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VOLUME I

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Preface

The material in these two volumes provides an up-to-date account of our understanding of the physical properties of solid surfaces. Research in this area has already attained a level of considerable sophistication, and surface science promises to continue to be an exciting and worthwhile field of endeavor in the foreseeable future. The various chapters critically examine the status of work on a number of aspects of solid surfaces and attempt to predict the most profitable avenues for future research. The spectacular increase in interest in surface physics, occurring in the last decade, has been sparked by the realization of the importance of surfaces and interfaces in solid state devices and chemical reactions. It is therefore an area of applied research; yet, as witnessed by numerous examples in this book, it is one that requires the techniques of both the materials engineer and the mathematical physicist.

The two volumes contain a set of papers carefully selected to give broad coverage of the field of surface physics. The individual chapters deal with topics of current research interest and have been chosen to emphasize surface properties rather than the applicability of experimental techniques. It is hoped that these volumes will be especially useful to research workers, teachers, and graduate students in surface physics as well as serving as reference texts for the materials scientist specializing in other branches of the subject.

The authors of the various chapters are all individuals who have made substantial contributions to the development of the particular areas about which they have written. In most cases emphasis has been placed on fundamentals and on those aspects that are least likely to require revision as the subject develops. I have found that editing this work has been an educational experience and can only hope that the reader will derive comparable benefits.

I am especially grateful to Aggie Sirrine, Marsha Leonard, and Karen Pratt for their assistance in preparing this volume for publication.

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Surface Crystallography

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I. INTRODUCTION

An understanding of the microscopic properties of materials is not possible without a precise knowledge of the positions of the atoms. In fact, a major contribution to the progress of chemistry and solid-state physics in this century has been the systematic determination of the structure of crystalline materials. This task was first made possible by x-ray crystallography. Since the development of x-ray techniques, neutron and high-energy-electron diffraction have become valuable supplements in structure determination. Early in the century diffraction techniques were used to determine the structures of simple crystals, and they have since been applied successfully to increasingly complicated alloy, organic, and biological materials.

In contrast, the precise knowledge of atomic arrangements on or near surfaces is in its infancy. As a consequence, our understanding of surface properties is rather meager. There are a wide variety of surface problems that cannot be attacked without a detailed knowledge of the surface structure. Thus, surface crystallography becomes the key to surface physics and chemistry. By *surface crystallography* we mean the study and determination of the arrangement of the atoms which make up the surface of crystalline materials. The *surface* is the transition region between the three-dimensional periodic structure of the bulk crystal and vacuum. Thus the surface includes all the layers of atoms that do not have the three-dimensional periodicity of the bulk. Surface structure denotes the arrangement of the atoms in the surface.

The present chapter is restricted to "crystalline" surfaces, which are defined as those which exhibit a two-dimensional periodicity in the surface plane. We discuss only ordered surfaces because ordered bulk solids have been found to be much simpler to understand than their amorphous counterparts; this is probably also true for surfaces. We cover three main subjects:

(1) a description of the possible types of surface structures and their symmetry and nomenclature;

(2) a discussion of low-energy electron diffraction (LEED), which is the appropriate diffraction technique for surface structure determination;

(3) a review of the surface structures which have been determined to date.

It is hoped that this chapter will be useful to readers with varying interests. Those whose primary interest is a brief overview of the subject and a knowledge of the surface structural information that has been obtained to date should find what they need in Sections II and VII. The student interested in the procedures of electron diffraction and surface structure determination should also read Sections III and V. The person who wishes to understand the theoretical basis of electron diffraction will find this treated in Sections IV and VI.

II. SURFACE STRUCTURES

A. Clean Surfaces

It will prove helpful, in what follows, to think of a clean surface in terms of a zero-order approximation, the so-called "ideal surface," an abstraction created by passing a plane (the surface plane) through an infinite crystal and separating the two parts to infinity. Usually it is assumed that the surface plane is, in fact, a low-index crystallographic plane that passes midway between atom centers; but this need not always be the case. The important point in the definition of an "ideal surface" is that it forbids any changes in the system other than the establishment of a different set of boundary conditions. Positions of the atoms and the electron density inside the semi-infinite crystal remain the same as in the original infinite crystal.

Of course, "ideal surfaces" do not exist in nature. The three-dimensional translational symmetry of the crystal is destroyed in the direction perpendicular to the surface plane, and, consequently, the wave functions of the electrons are modified in the vicinity of the surface. The resulting relaxation of electron charge density creates a new self-consistent potential in the surface region of which the principle component is a surface dipole. Physically this is plausible, as those electrons possessing a large kinetic energy can tunnel into the potential barrier created at the surface. The excess electron density outside and the uncompensated positive charge inside the surface create a surface dipole layer. The extent to which the electron gas penetrates into the vacuum can be estimated from the uncertainty principle as follows:

$$\Delta x \, \Delta p \cong \hbar$$

so that

$$\Delta x \cong \hbar/(2mE_F)^{1/2} \cong 1 \quad \text{Å}, \tag{1}$$

as the Fermi energy $E_F \cong 5\,\text{eV}$ for metals. Detailed self-consistent calculations of the electron density near metallic surfaces by various authors (Lang and Kohn, 1970; Appelbaum and Hamann, 1972) support the picture of the

conduction electron density in a metal passing from the bulk value to a rapidly decaying exponential tail with a characteristic length of approximately a lattice parameter.

In semiconductors and insulators where the description of the electron wave functions in terms of covalent and ionic bonds is more appropriate than in terms of an electron gas, the removal of the rest of the crystal (the formation of the surface) allows polarization of the bonds in the direction of the surface normal, again creating a dipole layer. Recent self-consistent calculations by Appelbaum and Hamann (1973) on Si confirm this picture.

In addition to the relaxation of the electrons, there is also relaxation of the atomic positions in the surface region. In the simplest case, the top layer of atoms is displayed directly toward or away from the layer underneath. Analysis of LEED data indicates that such displacements do indeed occur in surfaces of clean metals. Table III (in Section VII) gives the percentage relaxation of the outer plane for some metal surfaces as presently believed.

In surfaces of many semiconductors as well as a few metals, more complex atomic rearrangements occur. Clean surfaces apparently relax into structures which have translational symmetries parallel to the surface different from those of the bulk. These are the so-called "reconstructed surfaces." The structures of these surfaces are as yet undetermined, although numerous speculations exist. For example, several authors (Fedak and Gjostein, 1967; Palmberg and Rhodin, 1967, 1968) have found that the clean {001} surfaces of Au and Pt have structures different from the bulk and have suggested that the top layer of atoms on both surfaces is close-packed with hexagonal symmetry. Many semiconductors [Si and Ge, for example (Lander and Morrison, 1962, 1963; Lander et al., 1963)] have surfaces which give very complicated LEED patterns with large surface periodicities. Thus the clean surfaces of real crystals have structures which may result from either slight atomic motions perpendicular to the surface or complete rearrangements of the surface atoms into different crystallographic phases.

B. Overlayers and Surface Alloys

If atoms (usually other than the substrate's) are added to the surface plane, either from the vapor phase or by segregation of bulk impurities onto the surface, other surface structures can arise. These surface structures are due to: (1) ordered adsorption of up to a monolayer of atoms, (2) epitaxy, i.e., the growth of multilayered ordered structures; and (3) mixing of adatoms with surface atoms to form ordered surface alloys.

It is convenient to divide gas adsorption into two categories: (a) physical adsorption and (b) chemisorption. In the former, the heats of adsorption are typically of the order of 1 kcal/mole, the bond being due to van der Waals

interactions; chemisorption, on the other hand, involves larger heats of adsorption, the bond being ionic, covalent, or metallic in character.

Physical adsorption systems studied include the rare gases xenon on Ir (Ignatiev and Rhodin, 1973a) and argon, xenon, and krypton on Nb (Dickey *et al.*, 1970; Farrell *et al.*, 1972). As the heats of adsorption are low, these studies were carried out at low temperatures. The rare-gas atoms apparently adsorb on the substrate in a well-ordered, close-packed monolayer structure with no evidence of alloying. Obviously, the weakness of the overlayer–substrate bond is such as to favor monolayer or multilayer coverage rather than alloy structures. As would be expected from the weak bonds, the rare-gas overlayers show much instability to thermal excitation; and for this reason the temperature dependence of the degree of order of such structures has been of interest.

In contrast to the relatively few physisorption studies reported in the literature, there exists a vast amount of chemisorption work. The reader is referred to the excellent reviews by May (1970) and Somorjai and Farrell (1971); the latter have included an extensive table of the work done prior to 1971. The data summarized include the substrate and surface plane, the adsorbed gas, and the various structures found in terms of their two-dimensional translational periodicity. A definitive assignment of the atomic positions in each of the surface structures reported has not yet been made. All that has been determined is, in fact, the two-dimensional translational periodicity of the overlayer plus substrate. Indeed it is now the task of surface crystallographers to enlighten this very challenging field by utilizing the recent theoretical and computational advances in electron diffraction.

The possible chemisorbed structures fall into two more or less well-defined groups: those in which the adsorbed atoms form a periodic coherent layer on top of the substrate (overlayers) and those in which the interactions between the adatoms and the substrate atoms result in alloy-type structures. In both cases the most important questions to be answered by surface crystallography are (1) what is the size and the shape of the basic periodic unit (the unit mesh) of the surface, (2) what is the orientation of the surface mesh relative to the substrate, and (3) what is the number and the arrangement of atoms in the unit mesh? In the alloy case the two-dimensional periodicity may vary from layer to layer, as there exists a three-dimensional structure with composition and atomic arrangement varying as a function of distance into the crystal. These alloy structures can indeed be very complicated and more difficult to solve than the monolayer structures. Unfortunately, it is not presently possible to tell if a given surface has, in fact, a monolayer structure without subjecting it to a full analysis that allows for the possibility of an alloy. Estimates of surface coverage by Auger spectroscopy are not sufficiently precise and, in any event, cannot easily differentiate between atomic species

on the top layer or in the layer just below. Estimates of coverage by the evaporation of known amounts of adsorbate onto the substrate suffer from a lack of understanding of sticking coefficients. Measurements of adsorption and desorption by monitoring changes in ambient gas pressure cannot demonstrate with certainty that the atom in question is adsorbed on top of the substrate or incorporated in an alloy. Perhaps much more careful Auger analysis will eventually provide a useful answer independent of a full-scale structural determination by diffraction.

III. EXPERIMENTAL TECHNIQUES AND METHODS FOR SURFACE STRUCTURE DETERMINATION

A. General Considerations

A useful probe of the surface region must (1) have a characteristic wavelength small enough to resolve atomic dimensions, and (2) interact strongly with matter. The latter requirement is necessary to ensure that surface rather than bulk properties are investigated. Thus the ideal probe should have a mean free path of the order of several atomic layers, which is the commonly accepted thickness of most surface structures.

The above requirements restrict the choice of surface probes to (1) low energy (0–500 eV) electrons, (2) higher energy electrons (up to 100 keV) near grazing incidence, and (3) ion and atomic beams. The great bulk of work on surface structure analysis now in progress utilizes low-energy (and to a much lesser extent high-energy) electrons, and the theory and techniques of this probe will be the major concern of this chapter. For our purposes we exclude any discussion of the vast and enormously fruitful work done in field-ion and field-emission microscopy. Our justification for this omission is mainly that so far these techniques have not revealed structural information about any but the simplest surfaces. Furthermore, some of the most interesting surface structures are not stable in the high electric fields involved in field-ion microscopy. The subject is actually a special field in itself that requires more discussion than we can give here. We merely note that Graham and Ehrlich (1974) have determined the adsorption sites of single adatoms of tungsten on a W{111} surface by using field-ion microscopy.

Ion and atomic beam scattering should also be useful techniques for obtaining information about surface structure, but very little work has been done in this field. We may mention, however, that Brongersma (1974) has concluded from ion beam scattering that there is no Ni in the top layer of the $c(2 \times 2)$ structure of S on Ni{100}.

B. Electron Diffraction

At this time the most powerful and certainly the most promising technique for determining the atomic structures of solid surfaces is the diffraction of electrons and, in particular, low-energy electrons. Low energy is generally considered to be the range from 10 V to 500 eV. High-energy electrons in the 50 keV range at grazing angles (1 to 3°) to the surface (a probe called RHEED for Reflection High-Energy Electron Diffraction) offer an alternative to LEED. However, a serious disadvantage of RHEED is that the constraint of grazing incidence requires very flat surfaces that are difficult to obtain. For this reason Moon and Cowley (1972) have recently argued in favor of the medium energy range of electron energies (MEED) with angles of incidence somewhat larger than grazing. In all three techniques the component of the incident electron momentum vector perpendicular to the surface is of the same small order of magnitude. This ensures that the penetration of the electrons extends only through several layers, and thus the diffracted beams contain information of the surface region rather than the bulk.

We will next briefly describe a typical LEED experiment. An electron gun directs a beam of low-energy electrons onto the crystal sample. The energy spread in a typical system is ~0.5 eV and the angular divergence ~0.5°. These data imply a coherence width of the electron beam at the crystal of ~200–500 Å (Estrup and McRae, 1971). For this reason LEED cannot "see" features which have spatial extents greater than ~200 Å, and therefore it is sensitive only to small regions of the surface over which, fortunately, the periodicity of the surface is accurately maintained. Steps, kinks, and gross surface imperfections usually do not interfere with the diffraction from surface structures but manifest themselves as background "noise." The intensities and momenta of the electron beams backscattered from the crystal surface are measured as functions of energy (E) and angle of incidence (θ, ϕ) of the incident electron beam. The angle ϕ describes the rotation of the crystal about the surface normal and the angle θ the tilt of the surface normal away from the incident beam. Values of ϕ are usually, but not always, restricted to those for which the plane of the incident beam and the surface normal lie along a low-index crystallographic plane. Measurements of the intensities of the diffracted beams are made either directly by means of a Faraday cup or indirectly by determining the brightness of the light emission causes by post-acceleration of the diffracted electrons onto a fluorescent screen. Figure 1 illustrates the main features of the post-diffraction-acceleration-type LEED apparatus.

Obviously, an accurate characterization of the surface is of the utmost importance. Since roughly one monolayer per second of the ambient gaseous
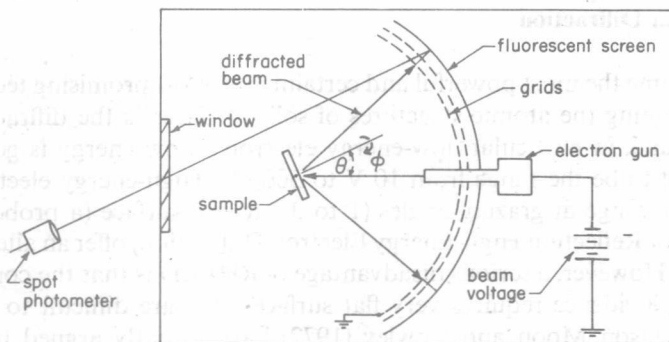
Fig. 1. Schematic drawing of display-type (or post-diffraction-acceleration-type) LEED apparatus. The outer grid (facing the sample) and the sample itself are usually held at ground potential so that the electrons travel in a field-free region. The inner grid is maintained at a negative potential a few volts below that of the incident beam and effectively cuts off the inelastically scattered electrons. The fluorescent screen is at a positive potential of several kV to accelerate the electrons to sufficient energy to excite the phosphor. The angles of incidence θ and ϕ are defined in the text.

species impinges on a surface at a pressure 10^{-6} Torr, it is necessary to work at least in the 10^{-10} Torr range in order to have sufficient time (about two hours) to perform an experiment without the crystal surface becoming contaminated.

Having made provisions for keeping the surface of the sample well characterized during an experiment, one must initially clean the surface "in situ," i.e., in the vacuum chamber of the LEED apparatus. Techniques used for this purpose include:

(a) cleavage of the crystal in vacuum, a method obviously limited to those materials and planes for which cleavage is possible, including many ionic and covalent materials but probably only a few metals, e.g., Be, Zn, Bi and Sb;

(b) heat treatments of the sample in vacuum to temperatures high enough to vaporize surface contaminants, a technique used successfully for cleaning refractory metals such as W and Nb;

(c) cycles of ion bombardments and anneals in vacuum (this technique has been found to be effective for almost all surfaces studied to date);

(d) heat treatments in oxidizing or reducing atmospheres.

The last method can be very time consuming; in some cases weeks of alternate heat treatments in hydrogen (or oxygen), ion bombardments, and anneals are necessary before all impurities that segregate to the surface from the bulk are removed.

If a surface has sufficient long-range order [usually a minimum of 10% of the surface must be well-ordered in regions whose dimensions are greater

than the coherence width of the electron beam (~ 200 Å)], the electrons scattered elastically from the surface form a LEED pattern on the fluorescent screen that is simply a projection of the reciprocal lattice of the substrate and surface taken together on the plane of the surface. This can be seen as follows. The potential in the vacuum is assumed to be zero. The substrate potential is three-dimensionally periodic, and its translational symmetry can be characterized by a three-dimensional reciprocal lattice. The surface region can be either a continuation of the substrate up to the surface plane or it can have its own two-dimensionally periodic structure. In the rest of this section we will assume, for simplicity, that the surface has the same two-dimensional periodicity as the bulk has in planes parallel to the surface. In the vacuum the solutions of the Schrödinger equation are plane waves whose energy is given by the square of the wave vector. In particular, the incident electron is represented by $e^{i\mathbf{k}\cdot\mathbf{r}}$. The wave vector $\mathbf{k}$ is separated into components parallel ($\mathbf{k}_\rho$) and perpendicular ($\mathbf{k}_z$) to the surface. The coordinates of the system are chosen in such a way that the crystal surface is the plane $z = 0$, with the z direction positive inside the crystal. If the angle between the incident wave vector $\mathbf{k}$ and the surface normal is denoted by θ and the energy by E, then

$$|\mathbf{k}_z| = E \cos\theta \quad \text{and} \quad |\mathbf{k}_\rho| = E \sin\theta. \quad (2)$$

(Atomic units are used throughout. The unit of energy is the rydberg, and distances are expressed in terms of Bohr radii, $\hbar = 1$, $2m = 1$, and $e^2 = 2$.) The potential (three-dimensional in the substrate, two-dimensional in the surface region, and zero in the vacuum) has two-dimensional periodicity everywhere. Thus, in the vacuum region, the incident electron is scattered into the plane waves

$$\psi_i^0 = \exp[i(-\mathbf{k}_{zi}' + \mathbf{k}_\rho + \mathbf{K}_i) \cdot \mathbf{r}], \quad (3)$$

which conserve energy and crystal momentum parallel to the surface up to a two-dimensional reciprocal lattice vector $\mathbf{K}_i$. For the simple surface assumed here, $\mathbf{K}_i$ is the projection on the surface plane of a three-dimensional reciprocal lattice vector of the bulk. The perpendicular component $\mathbf{k}_{zi}'$ of the ith scattered wave, the two-dimensional reciprocal lattice vector $\mathbf{K}_i$, and the energy are related by energy conservation:

$$\mathbf{k}_{zi}' = (E - |\mathbf{k}^\rho + \mathbf{K}_i|^2)^{1/2}. \quad (4)$$

The positive square root is taken to satisfy the boundary condition at minus infinity (i.e., one plane wave, the incident wave, propagates toward the crystal). For a given energy E and angle of incidence θ, the scattered waves can be grouped into a finite set of propagating waves with $\mathbf{k}_{zi}'$ real and an infinite set of evanescent waves with $\mathbf{k}_{zi}'$ imaginary. Writing the