

# Topics in Applied Physics

Volume 4

## Interactions on Metal Surfaces

Editor: R. Gomer

J. R. Smith Theory of Electronic Properties  
of Surfaces

S. K. Lyo and R. Gomer Theory of Chemisorption

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M. Boudart Concepts in Heterogeneous Catalysis



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With Contributions by

E. Bauer M. Boudart R. Gomer S. K. Lyo

D. Menzel E. W. Plummer L. D. Schmidt

J. R. Smith

With 112 Figures

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Professor ROBERT GOMER

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# Topics in Applied Physics    Volume 4



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## Preface

Surface phenomena encompass an important but enormously vast field. Any attempt to treat all or even a major portion of them in a book of this size is clearly impossible. I have selected metal surfaces and interactions on them, principally chemisorption, as the main topics of this book because they are of fundamental importance to almost all aspects of surface science and because progress, both theoretical and experimental is now very rapid in this field. Although catalysis goes considerably beyond the confines of the rest of the book a discussion of it has been included (Chapter 7) because of its intrinsic importance, its close relation to other subjects discussed here, and finally to indicate that there is more to interactions on surfaces than the adsorption of hydrogen on the (100) plane of tungsten.

To keep within the limits of this monograph-like series choices had to be made even within these restrictions. The intent of the book is to acquaint the reader with the theoretical underpinnings, the most important techniques currently being used to investigate metal surfaces and chemisorption, and finally to present some of the results of modern research in this area. It was necessary to omit a number of important topics, for instance field emission and field ion microscopy. In part, these omissions were based on the availability of reference books and review articles, and in part on the editor's sense of priorities for this particular book.

Chapter 1 discusses the electronic properties of surfaces, with emphasis on clean surfaces, largely from the point of view of W. KOHN and his school, and indicates how the linear response approach can be extended to treat chemisorption. Chapter 2 devotes itself specifically to the theory of chemisorption with emphasis on LCAO-MO methods, but includes some discussion of other approaches. Chapter 3 gives a very brief summary of the principal techniques used in chemisorption research but is mainly devoted to discussing what is known about a number of actual systems. Chapter 4 deals with various desorption techniques and the theory of such processes. Chapter 5 discusses the theory of electron spectroscopies, specifically field and photoemission, which provide insight into the electronic structure of surfaces and

adsorption complexes, and presents a number of quite recent results obtained by these techniques. Chapter 6 is devoted to a discussion of low energy electron diffraction and Auger phenomena, two of the most important techniques for characterizing the geometry of clean and adsorbate covered metal and semiconductor surfaces, and for determining chemical composition on the atomic scale. Chapter 7, as already pointed out, is devoted to a discussion of catalysis.

Discussions of specific adsorption systems occur not only in Chapter 3 but figure importantly also in Chapters 4 and 5. In some cases there is redundancy in subject matter, but generally not in point of view. This comes about because there is as yet a great deal we do not understand about chemisorption. It is rather recent in fact that there is essentially universal agreement on the experimental *facts* for a given system. It is hoped that the occasional disagreements in interpretation, honestly presented, will not confuse the reader and will serve to give him the true flavor of the current status of this field.

Chicago, January 1975

ROBERT GOMER

## Contributors

BAUER, ERNST

Physikalisches Institut, Technische Universität Clausthal,  
D-3392 Clausthal-Zellerfeld, Fed. Rep. of Germany

BOUDART, MICHEL

Department of Chemical Engineering, Stanford University,  
Stanford, CA 94305, USA

GOMER, ROBERT

The James Franck Institute, The University of Chicago,  
Chicago, IL 60637, USA

LYO, SUNG K.

The James Franck Institute, The University of Chicago,  
Chicago, IL 60637, USA

MENZEL, DIETRICH

Physik-Department, Technische Universität München,  
D-8046 Garching bei München, Fed. Rep. of Germany

PLUMMER, E. WARD

Department of Physics, University of Pennsylvania,  
Philadelphia, PA 19104, USA

SCHMIDT, LANNY D.

Department of Chemical Engineering and Materials Science,  
University of Minnesota, Minneapolis, MN 55455, USA

SMITH, JOHN R.

Research Laboratories, General Motors Technical Center,  
Warren, MI 48090, USA



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# 1. Theory of Electronic Properties of Surfaces

J. R. SMITH

With 21 Figures

Surface or interface electronic structure has been generally recognized as being of pivotal importance in many technologies: solid state and gaseous electronics, catalysis, adhesion, and corrosion—to name a few. Despite its practical importance, our fundamental understanding of surface electronic properties has been greatly overshadowed by progress in understanding the bulk.

There is good reason for this situation. Experimentally, microscopically clean surfaces have been difficult to obtain. Theoretically, the loss of symmetry in the direction perpendicular to the surface greatly complicates calculations.

Recently, there has been rapid progress in our understanding of surfaces, however. The commercial availability of vacuum systems capable of  $10^{-10}$  Torr as well as a number of analytical tools (see Chapters 3–6), have allowed experimentalists to obtain well characterized, clean surfaces. The well developed methods of bulk theory are being applied with encouraging success to the computation of many surface electronic properties.

In this chapter, it is hoped that the reader will obtain some feeling for the basic physical principles involved in the electronic properties of surfaces. It is not meant to be a review, however. Because of space limitations, we were not able to discuss surface energy determinations, but fortunately there is a recent review by LANG [1.1] (see also [1.2]). The reader interested in the companion field of adhesion is referred to the review of KRUPP [1.3] and the more recent theoretical efforts of FERRANTE and SMITH [1.4]. Small particle properties are related to those of solid surfaces, and for an introduction to the former we suggest the recently successful work of JOHNSON *et al.* [1.5]. Surface phonons are indirectly related to surface electronic properties, and we refer the interested reader to the review of WALLIS [1.6].

In Section 1.1, the subjects of surface states, continuum states, and local orbitals in the surface region are introduced via a simple example. Section 1.2 is devoted to the electron work function with results for a wide range of metals, including the effects of crystallinity and of fractional monolayers of adsorbed gases. Dielectric response,

including impurity screening, is discussed in Section 1.3 with application to chemisorbed hydrogen. Resonance levels, electron scattering cross sections, binding energies, vibrational modes, and electronic charge distributions are considered. In Subsection 1.4.1 the subject of surface states is treated, including recent theoretical results for the (111) plane of Si. In Subsection 1.4.2, surface plasmons are discussed. Experimental and theoretical results are given for Al, as examples. The nature of the charge fluctuation associated with the surface plasmon is investigated. The subject of the local density of states in the surface region is discussed in Section 1.5. Results for a Ni *d*-band are presented. Finally, Section 1.6 is devoted to a short description of the current status of surface calculations.

### 1.1. A Simple Example: Surface States, Continuum States, and Local Orbitals

As an introduction to surface electronic structure, consider the simple model surface [1.7] specified by the one-dimensional potential of Fig. 1.1. The potential repeats periodically throughout the bulk and then rises to the vacuum level, forming a surface barrier. This surface barrier may be considered the wall of the box containing the electrons within the solid. Within this surface barrier there is a well whose depth is less than that of the bulk wells. This is reminiscent of a

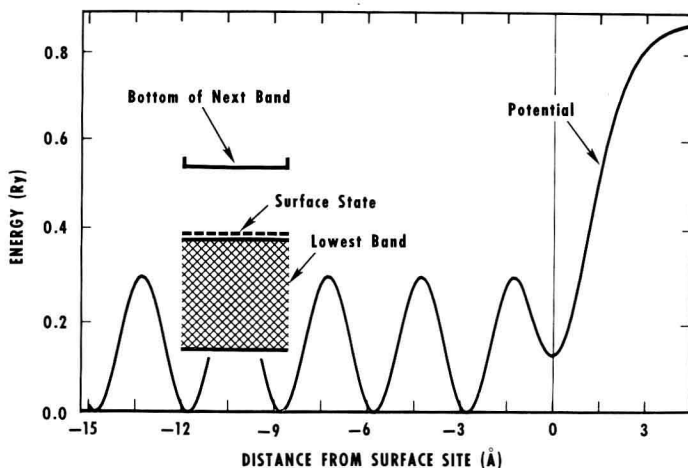


Fig. 1.1. Surface potential plot. The inset shows the relevant part of the energy spectrum of the potential [1.7]



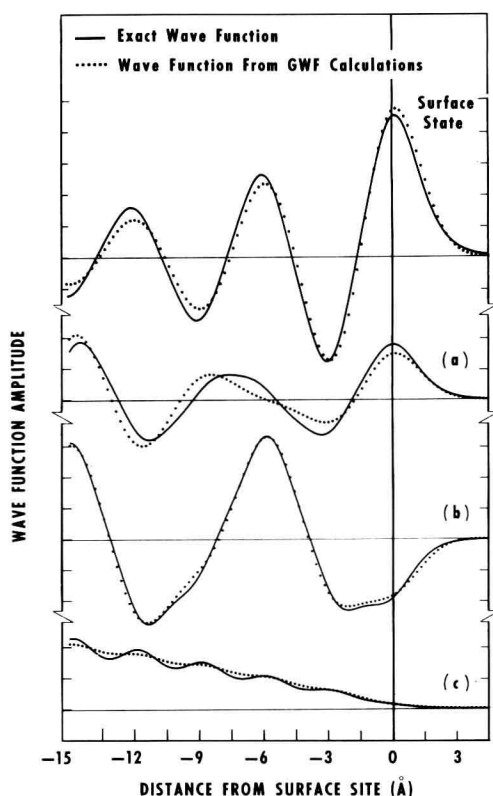


Fig. 1.2a-c. Top curves pertain to the surface state wave function, followed by examples of continuum states near to the top (a), middle (b), and bottom (c) of the lowest band [1.7]

chemisorbed layer, or an atomic layer of foreign particles which is chemically bonded to the surface.

There are two observations that can be made by inspection. The imposition of the surface barrier eliminates the periodicity in the direction perpendicular to the surface. Further, it is a quite strong and yet local perturbation.

The bulk bandwidth of the lowest band and the first band gap are also shown in Fig. 1.1. There is a surface state in the band gap. A surface state is an electronic state bound to the surface region. The local defect produced by the surface barrier can, under certain conditions, bind electrons.

Some of the wave functions of interest are plotted in Fig. 1.2. Let us consider some of the qualitative features of the wave functions.