

This book summarizes the present state of knowledge on the microscopic behaviour of oxide surfaces.

The first chapter of the book summarizes classical approaches, introduces the concept of ionicity, and describes the mixed ionic-covalent character of the oxygen cation bond in bulk materials. The next three chapters focus on the characteristics of the atomic structure (relaxation, rumpling and reconstruction effects), the electronic structure (band width, gap width, etc.) and the excitations of clean surfaces. Metal-oxide interfaces are considered in the fifth chapter with special emphasis on the microscopic interfacial interactions responsible for adhesion. The last chapter develops the concepts underlying acid-base reactions on oxide surfaces, which are used in catalysis, in adhesion science, and in colloid physics, and discusses their applicability to the adsorption of hydroxyl groups. A comprehensive list of references is included.

This book will be of interest to graduate students or researchers, to experimentalists and theorists in solid state physics, chemistry and physical chemistry.

Cambridge University Press
0521018579 - Physics and Chemistry at Oxide Surfaces
Claudine Noguera
Frontmatter
[More information](#)

Physics and Chemistry at Oxide Surfaces

Cambridge University Press
0521018579 - Physics and Chemistry at Oxide Surfaces
Claudine Noguera
Frontmatter
[More information](#)

PHYSICS AND CHEMISTRY AT OXIDE SURFACES

Claudine Noguera

Laboratoire de Physique des Solides, Orsay, FRANCE



Cambridge University Press
0521018579 - Physics and Chemistry at Oxide Surfaces
Claudine Noguera
Frontmatter
[More information](#)

CAMBRIDGE UNIVERSITY PRESS
Cambridge, New York, Melbourne, Madrid, Cape Town, Singapore, São Paulo

Cambridge University Press
The Edinburgh Building, Cambridge CB2 2RU, UK

Published in the United States of America by Cambridge University Press, New York

www.cambridge.org
Information on this title: www.cambridge.org/9780521472142

© Cambridge University Press 1996

This publication is in copyright. Subject to statutory exception
and to the provisions of relevant collective licensing agreements,
no reproduction of any part may take place without
the written permission of Cambridge University Press.

First published 1996
This digitally printed first paperback version 2005

A catalogue record for this publication is available from the British Library

Library of Congress Cataloguing in Publication data

Noguera, Claudine.
Physics and chemistry at oxide surfaces / Claudine Noguera.
p. cm.
Includes bibliographical references (p. –) and index.
ISBN 0 521 47214 8 (hardcover)
1. Surface chemistry. 2. Metallic oxides—Surfaces. I. Title.
QD506.N57 1996
546'.72153—dc20 95-48211 CIP

ISBN-13 978-0-521-47214-2 hardback
ISBN-10 0-521-47214-8 hardback

ISBN-13 978-0-521-01857-9 paperback
ISBN-10 0-521-01857-9 paperback

*Nuestras horas son minutos
Cuando esperamos saber,
Y siglos cuando sabemos
Lo que se puede aprender.*

Antonio Machado
Proverbios y Cantares
(Campos de Castilla)

*Hours are minutes
When we hope to know,
And centuries when we know
What can be learned.*

Contents

	<i>Preface</i>	xiii
1	Introduction	1
1.1	Classical models of cohesion	1
	The hard-sphere model	1
	Born's model and later developments	6
	Applications of the atomistic models	8
1.2	Origin of the insulating state	9
	Charge transfer oxides; correlated oxides	9
	Sawatzky–Zaanen's diagram and discussion	11
1.3	Ionicity of a chemical bond	13
	Thermo-chemical description	13
	Spectroscopic description	14
	The hetero-polar diatomic molecule (non-self-consistent treatment)	15
1.4	Bulk electronic structure of simple oxides	17
	Experimental techniques	17
	Theoretical techniques for electronic structure determination	19
	The alternating lattice model	24
	Band limits and band widths	28
	The gap width	33
	Ionic charges	34
	Cohesion energy	38
1.5	Conclusion	41
2	Atomic structure of surfaces	42
2.1	Preliminary remarks	42
	Notations	42
	Classification of surfaces	43
	Surface terminations	44

x	<i>Contents</i>	
	Criteria for surface stability	45
	Structural distortions	45
2.2	Experimental and numerical studies	47
	Rocksalt surfaces	47
	Rutile surfaces	48
	Perovskite surfaces	48
	Corundum surfaces	49
	Wurtzite surfaces	49
	α -quartz surfaces	49
	Steps and kinks on oxide surfaces	50
	Numerical studies	50
2.3	Relaxations	51
	Electrostatic mechanism	52
	Covalent mechanism	54
	Relaxation mechanism in mixed ionic-covalent systems	56
2.4	Rumpling	59
	Electrostatic mechanism	59
	Covalent mechanisms	63
2.5	Non-stoichiometric reconstructions	65
2.6	Conclusion	67
3	Electronic structure of surfaces	68
3.1	Experimental and theoretical studies	68
	Experimental studies	68
	Theoretical studies	70
3.2	Electronic structure of non-polar surfaces	71
	Madelung potentials and gaps	71
	Surface density of states	76
	Surface charges	78
	Electronic characteristics of thin films	84
	Surface energies	86
	Consequences of structural distortions on the electronic structure	88
3.3	Polar surfaces	91
	Polar and weakly polar surfaces	91
	Electrostatic arguments	92
	Electronic structure	95
	Synthesis	99
3.4	Non-stoichiometric surfaces	99
	Characteristics of the electronic structure	100
	Discussion	102
3.5	Conclusion	104

Contents xi

4	Surface excitations	106
4.1	Surface phonons	106
	Experimental and theoretical approaches	106
	Classification of the surface modes	107
	Rayleigh mode	109
	Fuchs and Kliewer modes	110
	Microscopic modes	111
	Soft phonons; reconstructions; structural phase transitions	112
4.2	Bulk electronic excitations	113
	General features	113
	Static $\omega = 0$ and macroscopic $q \rightarrow 0$ limits	114
	Static limit $\omega = 0$; spatial dependence of screening processes	115
	Dynamic screening $\omega \neq 0$; macroscopic limit $q \rightarrow 0$	116
	Local field effects	118
4.3	Surface dielectric constant	122
	Classical macroscopic limit	122
	A better account of the surface electronic structure	124
4.4	Conclusion	127
5	Metal–oxide interfaces	128
5.1	Introduction	128
5.2	First stages of deposition	131
	Atomic structure at the interface	132
	Metal electronic parameters	136
	Oxide stoichiometry	137
	Examples of interfacial compound formation	137
5.3	Wetting and adhesion	138
	General remarks	138
	Non-reactive interfaces	140
	Reactive interfaces	142
5.4	Theoretical analysis of the first stages of deposition	143
	Electronic structure of supported clusters	144
	Electronic structure of epitaxial monolayers	144
	Growth mode modelling	145
5.5	Description of a jellium–oxide interface	146
	The model	146
	Metal-induced gap states (MIGS)	147
	Charge transfer	147
	The Schottky barrier height	150
5.6	Interfacial energy	153
	Short-range repulsion energy	154
	Kinetic energy	154
	Electrostatic energy	155

xii	<i>Contents</i>	
	Exchange and correlation energy	157
5.7	Conclusion	159
6	Acid–base properties	160
6.1	Historical background	160
6.2	The acid–base concept in adhesion science	166
6.3	The acid–base concept in heterogeneous catalysis	170
6.4	Qualitative discussion	172
	Cation formal charge and ionic radius	173
	Cation electronegativity and oxygen charge	176
	First discussion of these parameters	178
	Mixed oxides	179
6.5	Hydroxyl groups on oxide surfaces	181
	Experimental results	181
	Theoretical results	183
	Charge transfers	185
	Density of states	190
	Adsorption energies	193
	Structural characteristics of hydroxyl groups	196
	Synthesis	200
6.6	Conclusion	201
	<i>References</i>	202
	<i>Index</i>	221

Preface

Although oxides have been the subject of active research for many years, they have attracted an increasing interest in the last decade. One reason for this interest is the discovery of superconductivity in copper oxide based materials, in 1986, with critical temperatures higher than the temperature of liquid nitrogen. Simple oxides have also been more thoroughly studied and a detailed analysis of their surface properties has been undertaken, thanks to several technological advances made during this period. The success in compensating charging effects, for example, has allowed spectroscopic measurements to be performed. Photoemission, x-ray absorption, Auger spectroscopy and low-energy electron diffraction now yield quantitative information, as they do for semi-conductors and metals. Topographic images of insulating surfaces can be recorded with an atomic force microscope. On the theoretical side, advanced numerical codes have been developed, which solve the electronic structure, optimize the geometry, and start accounting for dynamical effects in an *ab initio* way. The results presently available allow a first synthesis of the field.

The interest and the richness of the field of oxide surfaces lies in its inter-disciplinary nature and in the diversity of questions it raises, both on a fundamental and on an applied level. For example, geophysicists and geologists consider in detail the surface properties and porosity of the rocks of our earth, made of complex oxides whose properties are, to a large extent, controlled by the grain boundaries and internal surfaces. The mineral reactivity also interests the toxicologists, who try to understand the interactions between small particles and the biological medium. Small oxide particles may be found in colloidal suspensions, and the surface reactions, which take place at the interface with the solution, determine in a large part the nature and strength of the particle–particle interactions and thus the stability of the suspension. Oxides are also good catalysts, which are largely used, for example, in petrochemistry. Specific experimental

techniques have been developed to quantify the acidity or basicity of their surface sites and to establish a correlation between their catalytic activity and their surface geometry. In the multi-layered materials produced in modern industry, oxides are often used as supports for thin metallic films or grafted polymeric layers, as intercalation layers in electronic devices, etc. They are often present, although in an uncontrolled way, whenever a material is in contact with the ambient atmosphere. They play a fundamental role in corrosion processes and the surface properties of real materials, such as the friction coefficient, etc., are *in fine* determined by them. Finally, they offer a large field of investigations to surface physicists, who have developed concepts and obtained many results on metals and semi-conductor surfaces, but who are still trying to answer elementary questions on oxide surface characteristics – e.g. density of states, gap width, stoichiometry of the outer layers, reconstructions, defects.

In this vast context, the present book is restricted to well-defined themes, which have been the subject of recent developments and for which a microscopic understanding is emerging. The oxides which will be discussed are ‘simple’ insulating oxides, with cations from the four first columns of the periodic table or from one of the transition series, provided that they are in a closed-shell configuration – such as TiO_2 . Those oxides whose insulating character results from strong electron correlations will be discarded. Their *bulk* electronic structure remains a challenge for the theoreticians and little information on their surfaces is known. For a long time, all ‘simple’ insulating oxides were believed to be highly ionic, and were described by classical electrostatic models. More recently, electronic structure calculations have proved that most oxides are only partially ionic, but the relative weight of covalent and electrostatic interactions in these materials remains a subject of controversy. The first chapter of this book summarizes the classical approaches, makes a presentation of the concept of ionicity and proposes a quantum model, which accounts for the mixed ionic-covalent character of the oxygen-cation bonds in the bulk. The three following chapters focus on the atomic structure – relaxation, rumpling and reconstruction effects; the electronic structure – band width, gap width, etc.; and the excitations of clean surfaces. Interfaces between a metal and an oxide are considered in the fifth chapter, with a special stress put on the microscopic interfacial interactions responsible for adhesion. Although the relevance of some parameters to wetting and growth processes is indicated, all the kinetic aspects – growth of a metallic deposit on an oxide or superficial oxidation of a metal – are excluded. The last chapter develops the concepts underlying acid-base reactions, which are used in catalysis, in adhesion science and in colloid physics. It points out their relevance to chemisorption processes, and more specifically to the adsorption of hydroxyl groups on oxide surfaces.

Preface

xv

The aim of this book is to draw a panorama of the field, to ask questions, to indicate tracks for future research, rather than to present a final picture, which has still to be built up. Due to the connections with many disciplinary fields, it has not been possible to make an exhaustive bibliography. Many review papers or books are quoted, in which the reader will be able to trace the original papers. For the sake of synthesis and pedagogy, systematic features are stressed, relevant parameters are derived and a comparison is made between the concepts used in ‘this’ or ‘that’ research area. Theoretical models are proposed to synthesize the experimental or numerical results obtained on given systems and to obtain a consistent picture. Although they can only account for the gross features and the trends, they do represent an advance on the long way of the conceptualization of knowledge. The analytical support is highly inhomogeneous: some questions are developed at length; others are sketched only quickly and will leave the reader unsatisfied. It is the sign that much work remains to be done.

The French version of this book was written after a series of lectures given in 1992–3, in Orsay, to undergraduate students in solid state physics. The audience contained students preparing their theses, as well as researchers: solid state physicists, geophysicists, electrochemists and chemists, experimentalists or theoreticians. A special effort was thus made to settle the background necessary to a complete understanding, without assuming any advanced knowledge. I am deeply indebted to all the participants who encouraged me with their attendance and helped me with their questions. Many thanks are also due to my own PhD students who have shared my queries during the last years.

The final version of this book benefited greatly from discussions, comments and encouragements from some of my colleagues. Among them, I am especially grateful to J. Friedel, J. Jupille, S. and A. Chopin, P. Dubost, E. Ilisca, J. P. Pouget, J. P. Roux, A. Auroux and J. Schultz, who read part or the whole of the French draft, D. W. Jepsen who kindly read and corrected the English version, and C. Godrèche and P. Manneville whose help was invaluable in disentangling the subtleties of TEX formatting.

C. Noguera
Orsay, France