

# **The Chemical Physics of Surfaces**

## **SECOND EDITION**

**S. Roy Morrison**

*Simon Fraser University  
Burnaby, British Columbia, Canada*

**PLENUM PRESS · NEW YORK AND LONDON**



# Contents

<b>Notation . . . . .</b>	xv
<b>1. Introduction . . . . .</b>	1
1.1. Surface States and Surface Sites . . . . .	1
1.1.1. The Chemical versus Electronic Representation of the Surface . . . . .	1
1.1.2. The Surface State on the Band Diagram . . . . .	4
1.1.3. The Fermi Energy in the Surface State Model . . . . .	6
1.1.4. Need for Both Surface Site and Surface State Models . . . . .	6
1.2. Bonding of Foreign Species to the Solid Surface . . . . .	7
1.2.1. Types of Interaction . . . . .	7
1.2.2. The Chemical Bond . . . . .	10
1.2.3. Acid and Basic Surface Sites on Solids . . . . .	13
1.2.4. Adsorbate Bonding on Various Solid Types . . . . .	16
1.2.5. Movement of Surface Atoms: Relaxation, Reconstruction, and Relocation . . . . .	17
1.2.6. The Electronic Energy Level (Surface State) of a Sorbate/Solid Complex . . . . .	19
1.3. Surface Hydration on Ionic Solids . . . . .	20
1.4. Surface Heterogeneity . . . . .	22
<b>2. Space Charge Effects . . . . .</b>	25
2.1. General . . . . .	25
2.1.1. The Double Layer Involving Two Planar Sheets of Charge . . . . .	28

2.1.2.	The Space Charge due to Immobile Ions: The Depletion Layer . . . . .	29
2.1.3.	The Double Layer in the Band Diagram: Fermi Energy Pinning. . . . .	31
2.1.4.	The Double Layer at Electrical Contacts to the Semiconductor . . . . .	34
2.2.	Space Charge Effects with Reactive Surface Species . . . . .	35
2.2.1.	The Accumulation Layer. . . . .	38
2.2.2.	The Inversion Layer. . . . .	39
2.3.	Electron and Hole Transfer between the Solid and Its Surface . . . . .	40
2.3.1.	Basic Physical Model of Electron and Hole Capture or Injection. . . . .	41
2.3.2.	Electron and Hole Transfer with Large Changes in the Surface Barrier . . . . .	45
2.3.3.	Charge Transfer to a Surface Species in a Polar Medium: The Fluctuating Energy Level Mechanism . . . . .	47
<b>3.</b>	<b>Experimental Methods . . . . .</b>	<b>57</b>
3.1.	Semiconductor Space Charge Analysis: Surface States. . . . .	58
3.1.1.	Work Function. . . . .	59
3.1.2.	Surface Conductivity . . . . .	61
3.1.3.	Electroreflectance . . . . .	63
3.1.4.	Field Effect. . . . .	64
3.1.5.	Capacity of the Double Layer. . . . .	65
3.1.6.	Channel Measurements . . . . .	68
3.1.7.	Powder Conductance . . . . .	69
3.1.8.	Other Electrical and Optical Measurements. . . . .	71
3.2.	A Summary of Experimental Techniques . . . . .	72
3.3.	Energy Level, DOS, Measurement . . . . .	76
3.3.1.	Ultraviolet Photoelectron Spectroscopy (UPS, PES, ARUPS, ARPES, Two-Photon PES, Time-Resolved PES) . . . . .	76
3.3.2.	Inverse Photoelectron Spectroscopy (IPES, KRIKES) . . . . .	79
3.3.3.	Electron Energy Loss Spectroscopy (EELS, HREELS, REELS, EXELFS). . . . .	81
3.3.4.	Other Techniques . . . . .	82

3.4.	Measurement of Energy Levels for Electron Paris: Acidic or Basic Sites . . . . .	86
3.4.1.	Hammett Indicators . . . . .	87
3.4.2.	Adsorption of Gaseous Acids or Bases . . . . .	88
3.4.3.	Infrared Measurement of Lewis or Brønsted Sites . . . . .	88
3.5.	Measurement of Vibrational Levels, Plasmons . . . . .	89
3.5.1.	Infrared Absorption (IRRAS, RAIRS, MRIS, SEWS) . . . . .	89
3.5.2.	(High-Resolution) Helium Atom Scattering (HAS, HRHAS) . . . . .	92
3.5.3.	Other Techniques . . . . .	92
3.6.	Structure Analysis, Topography . . . . .	93
3.6.1.	Low-Energy Electron Diffraction (LEED) . . . . .	93
3.6.2.	Scanning Tunnel Microscopy or Spectroscopy, Constant Current Topography, Atomic Force Microscopy (STM, STS, CCT, AFM) . . . . .	96
3.6.3.	Impact Collision, Angle-Resolved, Ion Scattering Spectroscopy (ICISS, ARISS) . . . . .	98
3.6.4.	Surface Extended X-ray Absorption Fine Structure, Near-Edge X-ray Absorption Fine Structure (SEXAFS, NEXAFS) . . . . .	99
3.6.5.	Other Techniques for Structure Analysis . . . . .	101
3.7.	Composition Analysis . . . . .	104
3.7.1.	Auger Electron Spectroscopy, Scanning Auger Microscopy (AES, SAM) . . . . .	104
3.7.2.	Secondary Ion Mass Spectroscopy (SIMS) . . . . .	106
3.7.3.	Low-Energy Ion Scattering, Ion Scattering Spectroscopy (LEIS, ISS) . . . . .	106
3.7.4.	X-ray Photoelectron Spectroscopy, Electron Spectroscopy for Chemical Analysis (XPS, ESCA) . . . . .	108
3.7.5.	Other Techniques for Surface Composition Analysis . . . . .	109
3.8.	Adsorption/Desorption Kinetics and Adsorbate Bonding . . . . .	110
3.8.1.	Temperature-Programmed Desorption, Thermal Desorption Spectroscopy (TPD, TDS) . . . . .	110
3.8.2.	Electron Stimulated Desorption . . . . .	111
3.8.3.	Field Ion Microscopy (FIM) . . . . .	112
3.8.4.	Other Techniques for Studying Adsorption and Desorption . . . . .	114
3.9.	Miscellaneous . . . . .	114
3.9.1.	Modulated Beam Reaction Spectroscopy . . . . .	114
3.9.2.	Ellipsometry . . . . .	115
3.9.3.	Diffuse Scattering of Electrons . . . . .	116

3.9.4. Second Harmonic Generation in Laser Beams (SHG) . . . . .	116
3.9.5. Inelastic Electron Tunneling Spectroscopy (IETS) .	116
3.9.6. Electron Spin Resonance or Electron Paramagnetic Resonance (ESR or EPR) . . . . .	116
<b>4. The Adsorbate-Free Surface. . . . .</b>	<b>119</b>
4.1. Introduction . . . . .	119
4.1.1. The Classification of Solids . . . . .	119
4.1.2. Preparation of a Clean Surface . . . . .	121
4.2. Theoretical Models . . . . .	123
4.2.1. Quantum Models . . . . .	124
4.2.2. Semiclassical Models: The Madelung Model for Ionic Solids . . . . .	134
4.2.3. Models for Electron Pair Sharing: Lewis and Brønsted Sites . . . . .	138
4.2.4. Comparison of the Various Surface States and Sites	142
4.3. Measurements on Adsorbate-Free Ionic Solids. . . . .	146
4.3.1. Reconstruction on Solids. . . . .	146
4.3.2. Physical Measurements on Ionic Solids. . . . .	148
4.3.3. Chemical Measurements on Ionic Solids . . . . .	153
4.4. Measurements on Adsorbate-Free Covalent or Metallic Solids . . . . .	160
4.4.1. Reconstruction on Covalent and Metallic Solids .	160
4.4.2. Measurements of Intrinsic Surface States on Semi- conductors. . . . .	164
4.4.3. Measurements of Surface States and Surface Resonances on Metals . . . . .	170
<b>5. Bonding of Foreign Species at the Solid Surface. . . . .</b>	<b>173</b>
5.1. Reconstruction and Relocation in Bonding . . . . .	173
5.2. The Semiclassical Model of Bonding: The Surface Molecule . . . . .	175
5.2.1. Surface Molecule versus Rigid Band Model . . .	176
5.2.2. Adsorbate Bonds to Covalent or Metallic Solids .	178
5.2.3. Adsorbate Bonds to Ionic Solids . . . . .	185
5.2.4. Multilayer Adsorption: The Development of a New Phase . . . . .	187
5.3. Quantum Models of the Adsorbate/Solid Bond . . . . .	190
5.3.1. Solid State Theories: The Semi-infinite Crystal. .	191

5.3.2. Cluster Models . . . . .	192
5.3.3. Newns-Anderson Model . . . . .	194
5.3.4. Other Quantum Models . . . . .	198
5.3.5. Remarks . . . . .	198
5.4. Measurement of Adsorbate Surface States . . . . .	199
5.4.1. Screening Shifts and Other Inaccuracies in Measurement . . . . .	199
5.4.2. Bond Angles . . . . .	202
5.4.3. Surface State Energy Levels of Sorbate/Sorbent Bonds . . . . .	204
5.4.4. Vibrational Modes in Sorbate/Sorbent Bonding . . . . .	209
5.5. The Chemistry of Surface States . . . . .	210
5.5.1. Change of Surface State Energy Associated with Bonding . . . . .	210
5.5.2. The Influence of a Polar Medium or Coadsorbate on the Surface State Energy . . . . .	214
5.5.3. Surface States due to Multiequivalent Foreign Adsorbates . . . . .	215
5.6. The Formation of Surface State Bands . . . . .	218
<b>6. Nonvolatile Foreign Additives on the Solid Surface . . . . .</b>	<b>221</b>
6.1. General . . . . .	221
6.2. Dispersion of Additives . . . . .	222
6.2.1. Techniques for Dispersing Additives . . . . .	222
6.2.2. Measurement of Dispersion . . . . .	224
6.2.3. Sintering of Dispersed Particles: Surface Diffusion of Adsorbates . . . . .	225
6.3. The Cluster: The Transition between a Molecule and a Solid . . . . .	227
6.4. The Control of Surface Properties with Additives . . . . .	233
6.4.1. Theoretical Discussion . . . . .	233
6.4.2. Observations of Additive Effects . . . . .	237
6.4.3. Silane-Modified Surfaces . . . . .	247
6.5. The Real Surface . . . . .	247
<b>7. Adsorption and Desorption . . . . .</b>	<b>251</b>
7.1. Adsorption Isotherms and Isobars . . . . .	251
7.1.1. Physical Adsorption . . . . .	251

7.1.2.	Heat and Activation Energy of Adsorption, Irreversible Chemisorption . . . . .	255
7.1.3.	The Adsorbate Superstructure . . . . .	263
7.2.	Ionomerization on Semiconductors . . . . .	267
7.2.1.	The Surface State Representation of Adsorbed Species . . . . .	267
7.2.2.	Observations of Ionomerization . . . . .	274
7.3.	Adsorption with Local Bonding . . . . .	282
7.3.1.	Adsorption on Ionic Solids . . . . .	282
7.3.2.	Adsorption on Platinum . . . . .	288
7.3.3.	Coadsorption . . . . .	294
<b>8.</b>	<b>The Solid/Liquid Interface . . . . .</b>	<b>297</b>
8.1.	Introduction . . . . .	297
8.2.	Theory . . . . .	300
8.2.1.	Double Layers and Potentials in Electrochemical Measurements . . . . .	300
8.2.2.	Charge Transfer between the Solid and Ions in Solution . . . . .	305
8.2.3.	Energy Levels of Surface Species and Band Edges .	310
8.3.	Measurement Methods. . . . .	314
8.3.1.	Voltammetry, <i>C/V</i> Measurements . . . . .	315
8.4.	Measurements of Energy Levels and Band Edges. . . . .	319
8.4.1.	Measurement of $V_H$ . . . . .	319
8.4.2.	Measurement of Energy Levels of Surface Species .	320
8.4.3.	Measurement of the Reorganization Energy. . . . .	321
8.4.4.	Measurement of the Energies of Semiconductor Band Edges . . . . .	322
8.4.5.	Carrier Injection and Capture. . . . .	325
8.4.6.	Surface States due to Insoluble Species . . . . .	327
8.5.	Comparison of the Solid/Liquid Interface with the Solid/Gas Interface . . . . .	329
<b>9.</b>	<b>Photoeffects at Semiconductor Surfaces . . . . .</b>	<b>333</b>
9.1.	General . . . . .	333
9.2.	Simple Hole/Electron Recombination . . . . .	336
9.2.1.	Theory . . . . .	336
9.2.2.	Experimental Results . . . . .	338

9.3.	Photoadsorption and Photodesorption . . . . .	341
9.3.1.	Theory . . . . .	341
9.3.2.	Experimental Observations of Photoadsorption and Photodesorption . . . . .	346
9.4.	Photocatalysis . . . . .	351
9.4.1.	Photodecomposition of Adsorbed Species. . . . .	351
9.4.2.	Photostimulated Catalytic Reactions. . . . .	352
9.5.	Direct Excitation of Surface States by Photons. . . . .	354
9.6.	Photoeffects at the Semiconductor/Solution Interface . . . . .	358
9.6.1.	Photoelectrochemical Solar Cells, Photovoltaic Operation . . . . .	358
9.6.2.	Corrosion . . . . .	362
9.6.3.	Carrier Reactions at the Semiconductor Surface . .	364
9.6.4.	Reactions on Suspended Powders . . . . .	373
References . . . . .		375
Author Index . . . . .		405
Subject Index . . . . .		421