



## CONTENTS

CONTRIBUTORS . . . . .	xiii
FOREWORD . . . . .	xv
PREFACE . . . . .	xvii
LIST OF VOLUMES IN TREATISE. . . . .	xix
1. Work Function Measurements	
by L. W. SWANSON AND P. R. DAVIS	
1.1. Introduction . . . . .	1
1.2. Work Function Theory. . . . .	2
1.2.1. Basic Concepts . . . . .	2
1.3. Electron Emission Methods . . . . .	5
1.3.1. Thermionic Method . . . . .	5
1.3.2. Photoelectric Emission . . . . .	7
1.3.3. Field Electron Emission. . . . .	8
1.4. Retarding-Potential Methods . . . . .	11
1.4.1. The Shelton Triode . . . . .	11
1.4.2. Electron-Beam Method . . . . .	14
1.4.3. Field Emission Retarding-Potential Method. . . . .	15
1.5. Capacitance Methods . . . . .	17
1.5.1. The Kelvin-Zisman (Vibrating Capacitor) Method	17
1.5.2. Static Capacitor Methods . . . . .	19
1.6. Comparison of the Various Measuring Techniques. . . . .	19
1.7. Experimental Embodiments of the Various Techniques. .	21
1.8. The Future of Work Function Measurements. . . . .	22

<b>2. Vibrations in Overlayers</b>	
by W. HENRY WEINBERG	
2.1. Introduction . . . . .	23
2.2. Electron Energy Loss Spectroscopy . . . . .	31
2.2.1. Introduction . . . . .	31
2.2.2. Electron Energy Loss Spectrometers . . . . .	33
2.2.3. Theoretical Considerations . . . . .	46
2.2.4. Experimental Results: Dissociation of NO and Coadsorption of NO and CO on Ru(001) . . .	66
2.3. Reflection IR Spectroscopy . . . . .	75
2.3.1. Introduction . . . . .	75
2.3.2. Experimental IRAS . . . . .	76
2.3.3. Theoretical Considerations . . . . .	81
2.3.4. Experimental Results: The Adsorption of CO on Pd	84
2.4. Inelastic Electron Tunneling Spectroscopy . . . . .	95
2.4.1. Introduction . . . . .	95
2.4.2. Experimental Details . . . . .	96
2.4.3. Theoretical Concepts . . . . .	101
2.4.4. Experimental Results . . . . .	103
2.5. Conclusions . . . . .	113
2.5.1. Introduction . . . . .	113
2.5.2. CO Chemisorption on Ru(001) . . . . .	113
2.5.3. Tabulation of Previous EELS and IRAS Results .	121
2.5.4. Update	124
<b>3. Photoemission Spectroscopy of Valence States</b>	
by GIORGIO MARGARITONDO AND JOHN H. WEAVER	
3.1. Introduction: Three-Step Model, Escape Depth, Relevant Parameters	127
3.1.1. Photoemission: A Versatile Probe of the Valence States . . . . .	127

3.1.2. The Three-Step Model . . . . .	129
3.1.3. Escape Depth . . . . .	130
3.1.4. The Important Parameters. . . . .	132
3.2. Instrumentation. . . . .	133
3.2.1. Electron-Energy Analyzers. . . . .	134
3.2.2. Photon Sources . . . . .	140
3.3. Conventional Photoemission . . . . .	144
3.3.1. Density of States, Joint Density of States, and Energy Distribution of the Joint Density of States	145
3.3.2. Transition Probabilities . . . . .	146
3.3.3. Interpreting the Energy-Distribution Curves . . . . .	147
3.3.4. Processes without $\mathbf{k}$ Conservation . . . . .	148
3.3.5. Processing the Photoemission EDCs . . . . .	149
3.3.6. Experimental EDCs and Theoretical Curves: Bulk States	150
3.3.7. Surface-States Studies in the EDC Mode . . . . .	152
3.3.8. Adsorption States . . . . .	154
3.4. Polarized-Photon Photoemission . . . . .	156
3.4.1. Photon-Polarization Selection Rules. . . . .	156
3.4.2. Experimental Problems in the Photon-Polarization Techniques. . . . .	158
3.4.3. Photon-Polarization Effects in Angle-Resolved Photoemission: The Hermanson Rule . . . . .	159
3.5. Angle-Resolved Photoemission: The Band-Mapping Technique	161
3.5.1. The Surface Reciprocal-Lattice Vectors . . . . .	162
3.5.2. Mahan Cones . . . . .	163
3.5.3. Physical Information from the Angular Distribution of Photoelectrons . . . . .	164
3.5.4. Band-Structure Mapping for Two-Dimensional Crystals	165
3.5.5. Band Structure of Adsorbed Overlayers . . . . .	168
3.5.6. Three-Dimensional Band-Structure Mapping . . . . .	169
3.6. Synchrotron Radiation Techniques . . . . .	171
3.6.1. Constant-Final-Energy-State Spectroscopy and Partial-Yield Spectroscopy . . . . .	173

3.6.2. Constant-Initial-State Spectroscopy . . . . .	177
3.7. Conclusions and Future Prospects . . . . .	182
3.7.1. Future Prospects. . . . .	183
4. Core-Level Spectroscopies	
by ROBERT L. PARK	
4.1. Introduction . . . . .	187
4.2. The Core-Level Structure of Atoms . . . . .	188
4.2.1. Binding Energies. . . . .	189
4.2.2. Auger Yields and Lifetime Broadening. . . . .	190
4.3. The Interaction of Electrons with a Solid. . . . .	192
4.3.1. The Secondary-Electron Energy Distribution . . .	193
4.3.2. The Loss Spectrum. . . . .	195
4.3.3. The Emission Spectrum. . . . .	197
4.3.4. The Inelastic Scattering Mean Free Path . . . . .	198
4.4. Appearance-Potential Spectroscopy . . . . .	198
4.4.1. Core-Hole Excitation . . . . .	199
4.4.2. Background Suppression . . . . .	202
4.4.3. Resolution . . . . .	205
4.4.4. Soft-X-Ray Appearance-Potential Spectroscopy . .	207
4.4.5. Auger Electron Appearance-Potential Spectroscopy . . . . .	210
4.4.6. Disappearance-Potential Spectroscopy . . . . .	213
4.5. X-Ray Photoelectron Spectroscopy . . . . .	214
4.5.1. Core-Hole Excitation . . . . .	215
4.5.2. Electron Spectroscopy . . . . .	218
4.5.3. Chemical Shifts . . . . .	223
4.6. Comparison of Binding Energy Measurements . . . . .	225
4.7. Electron-Excited Auger Electron Spectroscopy . . . . .	226
4.7.1. The Auger Transition Energies . . . . .	227
4.7.2. The Auger Line Shape . . . . .	230
4.7.3. AES and Surface Composition . . . . .	231

4.8. Extended Fine Structure Analysis of Surfaces . . . . .	232
4.8.1. Surface-Extended X-Ray Absorption Fine Structure. . . . .	233
4.8.2. Extended Appearance-Potential Fine Structure . . . . .	235
5. Diffraction Techniques by MAX G. LAGALLY	
5.1. Introduction . . . . .	237
5.2. Elements of Diffraction Theory . . . . .	240
5.2.1. Diffraction from Surfaces . . . . .	242
5.2.2. Surface Defects . . . . .	245
5.3. The Measurement of Diffracted-Intensity Distributions . .	258
5.3.1. Sensitivity . . . . .	259
5.3.2. Resolving Power. . . . .	260
5.4. Surface Crystallography Measurements . . . . .	267
5.4.1. Diffraction Patterns . . . . .	267
5.4.2. Equilibrium Position Determinations . . . . .	268
5.4.3. Structural Defects . . . . .	272
5.4.4. Thermodynamics and Kinetics . . . . .	277
5.5. Instrumentation and Sample Preparation . . . . .	280
5.5.1. Electron Guns. . . . .	281
5.5.2. Detectors	283
5.5.3. Goniometers . . . . .	288
5.5.4. Sample Preparation . . . . .	289
5.6. Representative Experimental Results . . . . .	291
5.7. Conclusions . . . . .	297
6. Ion Scattering and Secondary-Ion Mass Spectrometry by W. HEILAND AND E. TAGLAUER	
6.1. Ion Scattering Spectrometry . . . . .	299
6.1.1. Fundamental Aspects. . . . .	299

6.1.2. Experiment. . . . .	312
6.2. Secondary-Ion Mass Spectrometry . . . . .	328
6.2.1. Fundamental Aspects. . . . .	328
6.2.2. SIMS Experiments. . . . .	337
6.3. Synopsis. . . . .	347
7. High-Field Techniques	
by J. A. PANITZ	
7.1. Field-Electron-Emission Microscopy . . . . .	349
7.1.1. The Fowler–Nordheim Equation . . . . .	350
7.1.2. The Field-Electron-Emission Microscope. . . . .	353
7.1.3. The Magnification of a Point-Projection Microscope. . . . .	357
7.1.4. The Resolution of a Point-Projection Microscope .	358
7.1.5. Adsorption Studies Using the FEEM . . . . .	359
7.1.6. Field Emission Energy Distributions. . . . .	361
7.2. Applications of Field-Electron-Emission Microscopy . .	363
7.2.1. Surface Diffusion . . . . .	363
7.2.2. Sputtering, Nucleation, and Electron Sources . .	366
7.2.3. Electrical Breakdown in High Vacuum. . . . .	368
7.2.4. Molecular Imaging. . . . .	370
7.2.5. Single-Atom Imaging. . . . .	374
7.3. Field-Ion Microscopy . . . . .	376
7.3.1. Field Ionization . . . . .	378
7.3.2. Field-Ion Energy Distributions . . . . .	380
7.3.3. The Hopping Gas Model . . . . .	383
7.3.4. The Low-Temperature Field-Ion Microscope . . .	384
7.3.5. The Magnification of a Field-Ion Image . . . . .	388
7.3.6. The Modern Field-Ion Microscope . . . . .	389
7.3.7. Microchannel-Plate Image Intensification . . . . .	390
7.3.8. Surface Diffusion Studies Using the FIM . . . . .	392
7.4. Field Evaporation . . . . .	397
7.5. Field-Ion Mass Spectroscopy . . . . .	399
7.5.1. Field Ionization Sources . . . . .	401

7.5.2. Liquid-Metal Field Desorption Sources . . . . .	402
7.6. Atom-Probe Mass Spectroscopy . . . . .	404
7.6.1. The Voltage-Pulsed Atom-Probe . . . . .	404
7.6.2. The Pulsed-Laser Atom-Probe . . . . .	406
7.6.3. Atom-Probe Measurements . . . . .	407
7.6.4. First-Layer Composition . . . . .	407
7.6.5. Composition of One Atomic Layer . . . . .	408
7.6.6. Average Composition of the Near-Surface Region .	411
7.7. Field-Desorption Microscopy . . . . .	412
7.7.1. The 10-cm Atom-Probe . . . . .	414
7.7.2. The Imaging Atom-Probe . . . . .	414
7.8. Molecular Imaging with Ions . . . . .	416
8. The Thermal Desorption of Adsorbed Species by JOHN T. YATES, JR.	
8.1. Introduction . . . . .	425
8.2. Early Studies of Desorption from Polycrystalline Substrates	427
8.2.1. Introduction . . . . .	427
8.2.2. Material Balance Equation for Thermal Desorption in a Vacuum System . . . . .	430
8.3. Thermal Desorption from Single Crystals . . . . .	431
8.3.1. Introduction . . . . .	431
8.3.2. Preparation, Mounting, and Temperature Programming of Single Crystals . . . . .	432
8.3.3. Isothermal Desorption Measurements . . . . .	436
8.3.4. Isosteric Heat of Adsorption . . . . .	438
8.3.5. Absolute Coverage Measurements . . . . .	441
8.3.6. Detectors for the Study of Thermal Desorption . .	444
8.4. Treatment of Experimental Desorption Data . . . . .	447
8.4.1. Desorption Kinetics Using Gas Evolution Measurements (Constant Rate of Heating) . . . . .	447
8.4.2. Desorption Kinetics Using Gas Evolution Measurements (Variable Rate of Heating) . . . . .	449

8.4.3. Coverage Measurements Made during Programmed Desorption . . . . .	451
8.4.4. Chemical Methods for Measuring Desorption Kinetics . . . . .	453
8.5. Theories of Thermal Desorption . . . . .	454
8.5.1. The Mobile Precursor Model in Adsorption and Desorption . . . . .	454
8.5.2. Statistical Thermodynamics of Adsorption and Desorption . . . . .	457
8.6. Concluding Remarks. . . . .	464
9. Experimental Methods in Electron- and Photon-Stimulated Desorption	
by THEODORE E. MADEY AND ROGER STOCKBAUER	
9.1. Theory and Mechanisms of Electron-Stimulated Desorption and the Relationship between ESD and PSD .	465
9.1.1. Experimental Observations . . . . .	465
9.1.2. Mechanisms of Ion Formation and Desorption . .	467
9.2. Experimental Methods in ESD and PSD . . . . .	473
9.2.1. Direct Detection of Desorbing Species . . . . .	473
9.2.2. Evaluation of ESD and PSD Data: Cross Sections and Electron-Induced Surface Damage . . . . .	498
9.2.3. Methods Based on Changes in Surface Properties: Detection of ESD and PSD Damage in Adsorbed Monolayers. . . . .	502
9.2.4. Measurements of Electron-Beam-Induced Damage in Thin Films and Bulk Samples . . . . .	505
9.2.5. Electron-Stimulated Adsorption . . . . .	511
9.3. Conclusions . . . . .	513
AUTHOR INDEX . . . . .	515
SUBJECT INDEX . . . . .	531

