

## Contents

Theory of Photoemission . . . . .	1
G. D. Mahan	
I. Introduction . . . . .	2
II. One Electron Theory . . . . .	2
A. History . . . . .	2
B. Atomic Photoionization . . . . .	3
C. Photoemission from a Solid . . . . .	8
D. Three Step Model . . . . .	11
III. Angular Dependence in Simple Metals . . . . .	12
A. Interband Transitions . . . . .	12
B. Internal Photoemission: Direction . . . . .	18
C. Internal Photoemission: Intensity . . . . .	20
D. Experiments on Ag . . . . .	23
IV. Plasmon Satellites in XPS . . . . .	29
A. X-ray Photoelectron Spectroscopy . . . . .	29
B. Electron Mean Free Path . . . . .	30
C. Extrinsic vs. Intrinsic . . . . .	34
V. Collective Effects . . . . .	40
A. Phonons . . . . .	40
B. Electron-Electron Interactions . . . . .	42
C. Auger Decay . . . . .	45
D. Auger and Phonon . . . . .	47
References . . . . .	51
The Use of Synchrotron Radiation in UPS: Theory and Results . . . . .	54
W. E. Spicer	
I. Introduction . . . . .	54
II. Characteristics and Benefits of Synchrotron Radiation . . . . .	56
III. Fundamentals of the Photoemission Process . . . . .	58
A. Introduction . . . . .	58
B. The Three-Step Model . . . . .	59
C. Effect of Various Scattering Events and Contribution of Scattered Electrons . . . . .	62

IV.	Benefits of Synchrotron Radiation in Photoemission Studies . . . . .	63
A.	Introduction . . . . .	63
V.	Tuning Synchrotron Radiation to Minimize Electron Escape Depth and Thus Maximize Surface Sensitivity . . . . .	65
A.	Introduction . . . . .	65
B.	GaAs Core Shifts Due to Oxygen Adsorption . . . . .	67
VI.	Use of Photon Energy Dependence of Absorption Cross Section to Separate Photoemission from Two Sources Which Are Degenerate in Energy . . . . .	72
A.	Introduction . . . . .	72
B.	"Missing" Bonding Orbitals of CO Adsorbed on Metal . . . . .	72
VII.	Angularly Resolved Photoemission Electron Spectroscopy (ARPES) . . . . .	76
A.	Introduction . . . . .	76
B.	Studies of CO Adsorbed on Ni(100) . . . . .	77
C.	Use of ARPES to Obtain Information of the Bulk Band Structure . . . . .	81
D.	Discussion of ARPES . . . . .	86
VIII.	Conclusions . . . . .	86
	References . . . . .	89
Angle Resolved Photoemission: Theoretical Interpretation of Results . . . . .		93
A. Liebsch		
I.	Introduction . . . . .	93
II.	The Excitation Process . . . . .	94
III.	Atoms . . . . .	99
IV.	Molecules . . . . .	104
1.	Gas Phase Molecules . . . . .	104
2.	Oriented Molecules . . . . .	107
V.	Adsorbates . . . . .	110
1.	Core Levels . . . . .	110
2.	Surface Molecules . . . . .	116
3.	Chemisorbed Overlayers . . . . .	119
VI.	Clean Surfaces . . . . .	125
1.	Formalism . . . . .	125
2.	TaS <sub>2</sub> . . . . .	131
3.	Cu(001) . . . . .	134
4.	Cu(111): Surface State . . . . .	137
	References . . . . .	141

Chemisorption and Catalysis on Metals: Applications of Surface Spectroscopies . . . . .	144
G. Ertl	
I. Characterization of Chemisorbed Systems . . . . .	144
1. The Molecular Nature of the Adsorbate . . . . .	144
2. The Surface Concentration (Coverage) . . . . .	147
3. Electronic Properties . . . . .	150
4. Structure of Chemisorbed Layers . . . . .	153
5. The Strength of the Substrate- Adsorbate Bond . . . . .	155
6. Vibrations . . . . .	157
II. Factors Influencing the Chemisorption Bond . . . . .	159
1. The Nature of the Substrate and Adsorbate . . . . .	159
2. The Local Character of the Chemisorption Bond . . . . .	159
3. The Crystallographic Orientation of the Surface . . . . .	162
4. The Role of Monoatomic Steps . . . . .	164
5. The Adsorption Site . . . . .	167
III. Interactions Between Adsorbed Particles . . . . .	169
IV. Dynamics of Surface Processes . . . . .	179
References . . . . .	186
X-Ray Photoelectron Spectroscopy of Solids . . . . .	192
G. K. Wertheim	
I. Introduction . . . . .	192
II. Valence Bands . . . . .	198
A. Metals and Alloys . . . . .	198
B. Compounds with Metallic Conductivity . . . . .	202
C. Insulators . . . . .	204
III. Photoemission from Open Shells . . . . .	205
A. The Rare Earths . . . . .	205
B. Transition Metal Compounds . . . . .	208
IV. Core Level Spectra . . . . .	211
A. Shake-Up Satellites . . . . .	212
B. Configuration Interaction . . . . .	213
C. Multiplet Splitting . . . . .	215
D. Many-Body Effects in Metals . . . . .	220
V. Summary . . . . .	223
References . . . . .	224
Current Problems in Auger Electron Spectroscopy . . . . .	230
T. E. Gallon	
Free Atom Auger Energies . . . . .	230
Auger Emission from Solids . . . . .	233

Auger Energies in the Solid State . . . . .	235
Chemical Shifts in Auger Spectra . . . . .	239
Line Broadening in the Solid State . . . . .	242
Auger Spectra Involving Band Electrons . . . . .	245
Quantitative Auger Spectroscopy . . . . .	260
References . . . . .	269
Studies of Adsorbate Electronic Structure Using Ion Neutralization and Photo- emission Spectroscopies . . . . . 273	
H. D. Hagstrum	
I. Introduction . . . . .	273
II. Electronic Transition Processes . . . . .	275
III. What We Can Learn from Studying Particle- Solid Electronic Interactions . . . . .	277
IV. Experimental Apparatus and Techniques . . . . .	278
V. Transition Rate and Probability Functions . . . . .	282
VI. The Auger Neutralization Process . . . . .	284
VII. Evidence for Variation of Atomic Energy Levels near a Surface . . . . .	288
VIII. Transition Rate Parameters for Auger Neutralization . . . . .	290
IX. Tunneling Processes for Unexcited Ions . . . . .	291
X. The Auger De-Excitation Process . . . . .	294
XI. Two-Stage Ejection Processes for Unexcited Ions . . . . .	296
XII. Two-Stage Ejection Processes for Excited Ions . . . . .	298
XIII. Oscillatory Ion Scattering from Surfaces . . . . .	302
XIV. Kinetic Ejection of Electrons by Ions . . . . .	304
XV. Energy Broadening in Auger Neutralization . . . . .	305
XVI. The Method of Ion Neutralization Spectroscopy (INS) . . . . .	309
XVII. What INS and UPS Measure . . . . .	314
XVIII. Adsorbate Electronic Structure . . . . .	317
XIX. Wave Function Variation Outside a Solid Surface . . . . .	319
XX. Uniqueness and Limitations of INS . . . . .	321
XXI. References . . . . .	322
Introduction to Secondary Ion Mass Spectrometry (SIMS) . . 324	
H. W. Werner	
1. Introduction . . . . .	324
2. Theory of SIMS . . . . .	328
2.1. Physical Basis . . . . .	328
2.2. Basic Formula for a SIMS Analysis . . . . .	338
2.3. Basic Experimental Embodiment . . . . .	353

CONTENTS

xi

2.4.	Type of Information Obtainable . . . . .	359
2.4.1.	Qualitative or Quantitative Survey Analysis . . . . .	359
2.4.2.	Surface Analysis . . . . .	359
2.4.3.	Depth Analysis . . . . .	359
2.4.4.	Element Mapping . . . . .	361
2.4.5.	Structural Analysis . . . . .	367
2.5.	Derived and Related Techniques . . . . .	372
2.5.1.	Neutral Particle Bombardment . . . . .	372
2.5.2.	Post Ionization of Sputtered Neutral Particles . . . . .	373
2.5.3.	Bombardment Induced Light Emission (BLE) . . . . .	374
2.5.4.	Laser Induced Ion Emission . . . . .	375
3.	Practice of Technique . . . . .	375
3.1.	Types of Instruments . . . . .	375
3.1.1.	Primary Ion Sources . . . . .	375
3.1.2.	Mass Analysers . . . . .	377
3.1.3.	Ion Detection . . . . .	393
3.1.4.	Use of Computers in SIMS Instrumentation . . . . .	407
4.	Comparison of SIMS with Other Thin Film Analytical Techniques . . . . .	416
	Conclusion . . . . .	422
	Appendix I . . . . .	423
	Appendix II . . . . .	433
	References . . . . .	436
	Author Index . . . . .	443
	Subject Index . . . . .	467