This graduate-level textbook covers the major developments in surface sciences of recent decades, from experimental tricks and basic techniques to the latest experimental methods and theoretical understanding. It is unique in its attempt to treat the physics of surfaces, thin films and interfaces, surface chemistry, thermodynamics, statistical physics and the physics of the solid/electrolyte interface in an integral manner, rather than in separate compartments. The Physics of Surfaces and Interfaces is designed as a handbook for the researcher as well as a study-text for graduate students in physics or chemistry with special interest in the surface sciences, material science, or the nanosciences. The experienced researcher, professional or academic teacher will appreciate the opportunity to share many insights and ideas that have grown out of the author's long experience. Readers will likewise appreciate the wide range of topics treated, each supported by extensive references. Graduate students will benefit from the elementary introductions to experimental techniques and the clear presentations of the theory behind the techniques and the phenomena. Wherever possible, physical concepts are emphasized and the mathematical notation kept to a minimum; the verbal explanations are supported by 350 graphs and illustrations.

ISBN 978-3-540-34709-5

› springer.com

1 Structure of Surfaces 1
1.1 Surface Crystallography 2
1.1.1 Diffraction at Surfaces 2
1.1.2 Surface Superlattices 7
1.2 Structure of Surfaces 12
1.2.1 Face Centered Cubic (fcc) Structures 12
1.2.2 Body Centered Cubic (bcc) Structures 17
1.2.3 Diamond, Zincblende and Wurtzite 19
1.2.4 Surfaces with Adsorbates 30
1.3 Defects at Surfaces 32
1.3.1 Line Defects 33
1.3.2 Point Defects 46
1.4 Observation of Defects 51
1.4.1 Diffraction Techniques 51
1.4.2 Scanning Microprobes 55
1.5 The Structure of the Solid/Electrolyte Interface 58

2 Basic Techniques 63
2.1 Ex-Situ Preparation 63
2.1.1 The Making of Crystals 63
2.1.2 Preparing Single Crystal Surfaces 65
2.2 Surfaces in Ultra-High Vacuum 71
2.2.1 UHV-Technology 71
2.2.2 Surface Analysis 81
2.2.3 Sample Preparation in UHV 88
2.3 Surfaces in an Electrochemical Cell 95
2.3.1 The Three-Electrode Arrangement 95
2.3.2 Voltammograms 97
2.3.3 Preparation of Single Crystal Electrodes 101

3 Basic Concepts 103
3.1 Electronic States and Chemical Bonding in Bulk Solids 103
3.1.1 Metals 103
3.1.2 Semiconductors 106
3.1.3 From Covalent Bonding to Ions in Solutions 109

3.2 Charge Distribution at Surfaces and Interfaces 112
3.2.1 Metal Surfaces in the Jellium Approximation 112
3.2.2 Space Charge Layers at Semiconductor Interfaces 116
3.2.3 Charge at the Solid/Electrolyte Interface 121
3.3 Elasticity Theory 125
3.3.1 Strain, Stress and Elasticity 125
3.3.2 Elastic Energy in Strained Layers 129
3.3.3 Thin Film Stress and Bending of a Substrate 132
3.4 Elastic Interactions Between Defects 139
3.4.1 Outline of the Problem 139
3.4.2 Interaction Between Point and Line Defects 142
3.4.3 Pattern Formation via Elastic Interactions 144

4 Equilibrium Thermodynamics 149
4.1 The Hierarchy of Equilibria 149
4.2 Thermodynamics of Flat Surfaces and Interfaces 152
4.2.1 The Interface Free Energy 152
4.2.2 Surface Excesses 158
4.2.3 Charged Surfaces at Constant Potential 161
4.2.4 Maxwell Relations and Their Applications 164
4.2.5 Solid and Solid-Liquid Interfaces 168
4.3 Curved Surfaces and Surface Defects 172
4.3.1 Equilibrium Shape of a Three-Dimensional Crystal 172
4.3.2 Rough Surfaces 180
4.3.3 Step Line Tension and Stiffness 184
4.3.4 Point Defects 187
4.3.5 Steps on Charged Surfaces 188
4.3.6 Point Defect on Charged Surfaces 194
4.3.7 Equilibrium Fluctuations of Line Defects and Surfaces 196
4.3.8. Islands Shape Fluctuations 201

5 Statistical Thermodynamics of Surfaces 207
5.1 General Concepts 207
5.1.1 Internal Energy and Free Energy 207
5.1.2 Application to the Ideal Gas 208
5.1.3 The Vapor Pressure of Solids 210
5.2 The Terrace-Step-Kink Model 211
5.2.1 Basic Assumptions and Properties 211
5.2.2 Step-Step Interactions on Vicinal Surfaces 215
5.2.3 Simple Solutions for the Problem of Interacting Steps 218
5.2.4 Models for Thermal Roughening 221
5.2.5 Phonon Entropy of Steps 223
5.3 The Ising-Model 225
5.3.1 Application to the Equilibrium Shape of Islands 225
5.3.2 Further Properties of the Model 228

5.4. Lattice Gas Models 233
5.4.1 Lattice Gas with No Interactions 233
5.4.2 Lattice Gas or Real 2D-Gas? 235
5.4.3 Segregation 238
5.4.4 Phase Transitions in the Lattice Gas Model 240

6 Adsorption 245
6.1 Physisorption and Chemisorption – General Issues 245
6.2 Isotherms, Isosters, and Isobars 254
6.2.1 The Langmuir Isotherm 254
6.2.2 Lattice Gas with Mean Field Interaction – the Fowler-Frumkin Isotherm 255
6.2.3 Experimental Determination of the Heat of Adsorption ... 260
6.2.4 Underpotential Deposition 264
6.2.5 Specific Adsorption of Ions 269
6.3 Desorption 273
6.3.1 Desorption Spectroscopy 273
6.3.2 Theory of Desorption Rates 276
6.4 The Chemical Bond of Adsorbates 284
6.4.1 Carbon Monoxide (CO) 284
6.4.2 Nitric Oxide 287
6.4.3 The Oxygen Molecule 288
6.4.4 Water 289
6.4.5 Hydrocarbons 291
6.4.6 Alkali Metals 295
6.4.7 Hydrogen 300
6.4.8 Group IV-VII Atoms 303

7 Vibrational Excitations at Surfaces 309
7.1 Surface Phonons of Solids 309
7.1.1 General Aspects 309
7.1.2 Surface Lattice Dynamics 312
7.1.3 Surface Stress and the Nearest Neighbor Central Force Model 315
7.1.4 Surface Phonons in the Acoustic Limit 317
7.1.5 Surface Phonons and Ab-Initio Theory 319
7.1.6 Kohn Anomalies 321
7.1.7 Dielectric Surface Waves 323
7.2 Adsorbate Modes 327
7.2.1 Dispersion of Adsorbate Modes 327
7.2.2 Localized Modes 330
7.2.3 Selection Rules 333
7.3 Inelastic Scattering of Helium Atoms 339
7.3.1 Experiment 339
7.3.2 Theoretical Background 342

7.4 Inelastic Scattering of Electrons 347
7.4.1 Experiment 347
7.4.2 Theory of Inelastic Electron Scattering 351
7.5 Optical Techniques 362
7.5.1 Reflection Absorption Infrared Spectroscopy 362
7.5.2 Beyond the Surface Selection Rule 366
7.5.3 Special Optical Techniques 369
7.6 Tunneling Spectroscopy 373

8 Electronic Properties 379
8.1 Surface Plasmons 379
8.1.1 Surface Plasmons in the Continuum Limit 379
8.1.2 Surface Plasmon Dispersion and Multipole Excitations ... 381
8.2 Electron States at Surfaces 383
8.2.1 General Issues 383
8.2.2 Probing Occupied States – Photoemission Spectroscopy... 386
8.2.3 Probing Unoccupied States 391
8.2.4 Surface States on Semiconductors 394
8.2.5 Surface States on Metals 401
8.2.6 Band Structure of Adsorbates 407
8.2.7 Core Level Spectroscopy 410
8.3 Quantum Size Effects 413
8.3.1 Thin Films 413
8.3.2 Oscillations in the Total Energy of Thin Films 417
8.3.3 Confinement of Surface States by Defects 420
8.3.4 Oscillatory Interactions between Adatoms 425
8.4 Electronic Transport 427
8.4.1 Conduction in Thin Films – the Effect of Adsorbates 427
8.4.2 Conduction in Thin Films – the Solution of the Boltzmann Equation 431
8.4.3 Conduction in Space Charge Layers 435
8.4.4 From Nanowires to Quantum Conduction 437

9 Magnetism 445
9.1 Magnetism of Bulk Solids 445
9.1.1 General Issues 445
9.1.2 Magnetic Anisotropy of Various Crystal Structures 447
9.2 Magnetism of Surfaces and Thin Film Systems 451
9.2.1 Experimental Methods 451
9.2.2 Magnetic Anisotropy in Thin Film Systems 455
9.2.3 Curie Temperature of Low Dimensional Systems 459
9.2.4 Temperature Dependence of the Magnetization 463
9.3 Domain Walls 467
9.3.1 Bloch and Néel Walls 467
9.3.2 Domain Walls in Thin Films 468
9.3.3 The Internal Structure of Domain Walls in Thin Films 470

9.4 Magnetic Coupling in Thin Film Systems 473
9.4.1 Exchange Bias 473
9.4.2 The GMR Effect 476
9.4.3 Magnetic Coupling Across Nonmagnetic Interlayers 479
9.5 Magnetic Excitations 482
9.5.1 Stoner Excitations and Spin Waves 482
9.5.2 Magnetostatic Spin Waves at Surfaces and in Thin Films.. 485
9.5.3 Exchange-Coupled Surface Spin Waves 486

10 Diffusion at Surfaces 491
10.1. Stochastic Motion 491
10.1.1 Observation of Single Atom Diffusion Events 491
10.1.2 Statistics of Random Walk 495
10.1.3 Absolute Rate Theory 498
10.1.4 Calculation of the Prefactor 500
10.1.5 Cluster and Island Diffusion 503
10.2 Continuum Theory of Diffusion 505
10.2.1 Transition from Stochastic Motion to Continuum Theory.. 505
10.2.2 Smoothening of a Rough Surface 508
10.2.3 Decay of Protrusions in Steps and Equilibration of Islands after Coalescence 511
10.2.4 Asaro-Tiller-Grinfeld Instability and Crack Propagation... 514
10.3 The Ehrlich-Schwoebel Barrier 518
10.3.1 The Concept of the Ehrlich-Schwoebel Barrier 518
10.3.2 Mass Transport on Stepped Surfaces 520
10.3.3 The Kink Ehrlich-Schwoebel Barrier 522
10.3.4 The Atomistic Picture of the Ehrlich-Schwoebel Barrier .. 523
10.4 Ripening Processes in Well-Defined Geometries 525
10.4.1 Ostwald Ripening in Two-Dimensions 525
10.4.2 Attachment/Detachment Limited Decay 530
10.4.3 Diffusion Limited Decay 532
10.4.4 Extension to Noncircular Geometries 535
10.4.5 Interlayer Transport in Stacks of Islands 536
10.4.6 Atomic Landslides 538
10.4.7 Ripening at the Solid/Electrolyte Interface 540
10.5 The Time Dependence of Step Fluctuations 542
10.5.1 The Basic Phenomenon 542
10.5.2 Scaling Laws for Step Fluctuations 544
10.5.3 Experiments on Step Fluctuations 550

11 Nucleation and Growth 555
11.1. Nucleation under Controlled Flux 556
11.1.1 Nucleation 556
11.1.2 Growth Without Diffusion 561
11.1.3 Growth with Hindered Interlayer Transport 565
11.1.4 Growth with Facile Interlayer Transport 567

11.2 Nucleation and Growth under Chemical Potential Control 572
11.2.1 Two-Dimensional Nucleation 572
11.2.2 Two-Dimensional Nucleation in Heteroepitaxy 574
11.2.3 Three-Dimensional Nucleation 576
11.2.4 Theory of Nucleation Rates 580
11.2.5 Rates for 2D- and 3D-Nucleation 587
11.2.6 Nucleation Experiments at Solid Electrodes 593
11.3 Nucleation and Growth in Strained Systems 597
11.3.1 2D-Nucleation on Strained Layers 597
11.3.2 3D-nucleation on Strained Layers 600
11.4 Nucleation-Free Growth 603
11.4.1 The Steady State Concentration Profile 603
11.4.2 Step Flow Growth 605
11.4.3 Meander Instability of Steps 607

Appendix: Surface Brillouin Zones 613

References 615

Subject Index 635

List of Common Acronyms 645