

Surface Structure Determination by LEED and X-rays

WOLFGANG MORITZ

University of Munich

MICHEL A. VAN HOVE

Hong Kong Baptist University



CAMBRIDGE
UNIVERSITY PRESS

Contents

	<i>Preface</i>	<i>page xi</i>
	<i>List of Abbreviations</i>	xiv
	<i>List of Major Symbols</i>	xix
	<i>Glossary</i>	xxiii
1	Introduction	1
	1.1 Brief Historical Background	1
	1.2 Physical Basis of LEED and SXRD	2
	1.3 Organisation of This Book	3
	1.4 Comparison of Some Surface Structure Techniques	4
2	Basic Elements	6
	2.1 Surface Geometry	6
	2.1.1 3-D Lattices	6
	2.1.1.1 Symmetry Operations	8
	2.1.2 Bravais Lattices	10
	2.1.3 Miller Indices	10
	2.1.4 2-Dimensional Lattices	13
	2.1.5 Reciprocal Lattice	16
	2.1.6 2-D Space Groups	19
	2.1.7 Atomic Positions	20
	2.1.8 Symmetry Operators in 2-D Space Groups	22
	2.1.9 Lattice Transformations	23
	2.1.10 Transformation of Reflection Indices	27
	2.1.11 Description of Superlattices	28
	2.1.12 Stepped Surfaces	30
	2.1.12.1 Direction of Step Edges	37
	2.1.12.2 Determination of Step Microfacets	38
	2.1.12.3 Determination of Step-to-Step Translation Vectors	39
	2.2 Diffraction from Surfaces	42
	2.2.1 Kinematic Theory of Diffraction	44
	2.2.2 X-ray Diffraction	48
	2.2.3 Electron Diffraction	50
	2.2.4 Ewald Construction for Diffraction from Surfaces	52

3	LEED Experiment	57
	3.1 Experimental Setup	57
	3.2 Diffraction Geometry	60
	3.3 Measurement of LEED Intensities	63
	3.3.1 Sample Preparation	63
	3.3.2 Accurate Alignment	65
	3.3.3 Measurement of LEED Intensities with a Video System	71
	3.4 Instrumental Response Function	74
	3.5 Brief Overview of Types of Available LEED Systems	75
	3.6 High-Resolution Instruments	77
	3.6.1 Spot Profile Analysis LEED (SPA-LEED)	77
	3.6.2 Low-Energy Electron Microscopy (LEEM)	80
	3.7 Some Developments for Special Applications	82
	3.7.1 In-situ Observation of Adsorption Processes	82
	3.7.2 Nanostructures	82
	3.7.3 Convergent Beam LEED	83
	3.7.4 Ultrafast Measurements	83
4	Interpretation of the Diffraction Pattern	85
	4.1 Symmetry and Orientation of the Unit Cell	86
	4.1.1 Domains due to Different Substrate Terminations	88
	4.1.2 Twin Domains in Structures with Superlattices	90
	4.1.3 Glide Planes	91
	4.2 Determination of the Lattice Constant	93
	4.3 Correction of the Incidence Angle	94
	4.4 Stepped Surfaces	95
	4.5 Faceted Surfaces	99
	4.6 Antiphase Boundaries	102
	4.7 Modulated Layers	107
5	LEED Theory: Basic Formalisms	110
	5.1 Diffraction Geometry	110
	5.2 Scattering Theory	114
	5.2.1 Atomic Scattering: Phase Shifts	115
	5.2.2 Multiple Scattering: Plane Waves and Spherical Waves	117
	5.2.3 Multiple Scattering in a Cluster of Atoms	118
	5.2.4 Multiple Scattering in Nanoparticles: NanoLEED	122
	5.2.4.1 The Sparse-Matrix Canonical Grid Method	123
	5.2.4.2 The UV Method	124
	5.2.4.3 NanoLEED for Nanoparticles	125
	5.2.4.4 NanoLEED with Matrix Inversion in Subclusters	127
	5.2.5 Multiple Scattering in Atomic Layers	129
	5.2.5.1 A Periodic Plane of Atoms	129
	5.2.5.2 Several Periodic Planes of Atoms	130

5.2.5.3	Diffraction Matrices for a Bravais-Lattice Layer	131
5.2.5.4	Diffraction Matrices for a Layer with N Periodic Atomic Planes	132
5.2.5.5	Layer Reflection and Transmission Matrices	133
5.2.6	Layer Stacking	133
5.2.6.1	Bloch Wave and Transfer Matrix Methods	133
5.2.6.2	Layer-by-Layer Stacking	136
5.2.6.3	Layer Doubling	138
5.2.6.4	Renormalised Forward Scattering (RFS)	139
5.2.6.5	The Case of Stepped Surfaces	140
5.2.6.6	Beam Subsets Independent in the Bulk	141
5.3	Symmetry in Calculations	142
5.3.1	Symmetry in Reciprocal Space	144
5.3.2	Symmetry in Angular Momentum Space	148
5.4	Approximations	151
5.4.1	Tensor LEED Approximation	151
5.4.2	Frozen LEED Approximation	156
5.4.3	Diffuse LEED for Disordered Surfaces	159
5.5	Thermal Effects	163
5.5.1	Thermal Vibration in the Kinematic Theory of Diffraction	164
5.5.2	Thermal Parameters	167
5.5.3	Harmonic Vibrations	168
5.5.4	Anharmonic Vibrations	169
5.5.5	Multiple Scattering Theory of Thermal Effects	172
5.5.6	Multipole Expansion Coefficients for Harmonic Vibrations	177
5.5.7	Multipole Expansion Coefficients for Anharmonic Vibrations	179
5.5.8	Example: Cu(110)	181
5.5.9	Example: Ru(0001)+($\sqrt{3}\times\sqrt{3}$)R30°-CO	182
5.6	From Calculated Amplitudes to Intensities	185
LEED Theory: Applications		188
6.1	Quantitative Structure Analysis	188
6.1.1	Approaches to Obtain Structural Information Directly from LEED Intensities	190
6.1.1.1	Averaging Methods and the Patterson Function	190
6.1.1.2	Holography	191
6.1.1.3	Further Approaches	195
6.1.2	Comparison of Measured and Calculated $I(V)$ Curves	195
6.1.3	Error Estimates	201
6.1.4	Optimum Energy Range	205
6.1.5	Structure Analysis Methods	206
6.1.5.1	Local Optimisation Methods	207
6.1.5.2	Global Search Methods	211

6.1.6	Influence of Non-structural Parameters on the Structure Determined by LEED	220
6.1.6.1	The Conventional Muffin-Tin Model	222
6.1.6.2	An Improved Muffin-Tin Model	225
6.1.6.3	A New Step-Free Overlapping Muffin-Tin Potential	226
6.1.6.4	Energy Dependence of the Inner Potential	233
6.1.6.5	Inelastic Mean Free Path (IMFP)	234
6.2	Quasicrystals	238
6.2.1	Quasicrystalline Order	239
6.2.2	Structural Principles of Quasicrystals	243
6.2.3	Diffraction from Quasicrystalline Surfaces	246
6.2.4	Quantitative Analysis of Quasicrystalline Surfaces	248
6.3	Modulated Surfaces	254
6.3.1	Principles of Modulated Structures	256
6.3.2	Examples of Modulated Surfaces	259
6.3.3	Identification of Modulated Lattices from STM Images	264
6.3.4	Reflection Indexing	272
6.3.5	Modulation Functions	275
6.3.6	Symmetry Restrictions of the Modulation	278
6.3.7	Diffraction from Modulated Surfaces	279
6.3.8	Multiple Scattering Effects in LEED from Modulated Structures	283
7	Surface X-ray Diffraction	285
7.1	X-ray Diffraction Methods	286
7.1.1	General Properties of X-ray Scattering	287
7.1.2	Reflection and Transmission of X-rays	290
7.1.3	Reflection and Transmission Coefficients near the Critical Angle	295
7.1.4	X-ray Diffraction at Grazing Incidence	298
7.2	Experimental Setup	303
7.2.1	Diffractometer Types	305
7.2.2	Measurement	308
7.2.3	Examples of Surface X-ray Diffractometers at Synchrotron Sources	318
7.2.4	Examples of Surface X-ray Diffractometers for Use As Laboratory Sources	328
7.2.5	Synchrotron Radiation Facilities	329
7.3	Data Analysis	330
7.3.1	Patterson Function	332
7.3.2	Direct Methods for Surface Structure Analysis	334
7.3.3	Coherent Bragg Rod Analysis (COBRA)	336
7.3.4	Modulus Sum Function (MSF)	341

7.3.5	Phase and Amplitude Recovery and Diffraction Image Generation Method (PARADIGM)	345
7.3.6	Difference Map Using the Constraints of Atomicity and Film Shift (DCAF)	356
7.3.7	Perturbation Method of Analysis of Density Profiles from Crystal Truncation Rod Data	358
7.3.8	Further Methods for Experimental Phase Determination	360
	<i>Appendices</i>	362
	<i>Appendix A Lists of Books Related to Surface Science</i>	363
	A.1 <i>General Books and Proceedings</i>	363
	A.2 <i>Books and Proceedings on Phenomena</i>	364
	A.3 <i>Books and Proceedings on Techniques</i>	365
	<i>Appendix B Lists of Surface Science Websites, LEED Codes and Related Data</i>	367
	B.1 <i>General Websites</i>	367
	B.2 <i>Website Related to Surface Structures</i>	367
	B.3 <i>Websites Related to Techniques</i>	367
	B.4 <i>LEED Codes and Related Data</i>	367
	B.4.1 <i>Structure Determination from LEED Intensities</i>	367
	B.4.2 <i>Experimental I(V) Curve Generation from LEED Patterns</i>	369
	B.4.3 <i>LEED I(V) Data</i>	369
	B.4.4 <i>Surface Structure Data</i>	369
	B.4.5 <i>LEED Pattern Simulation</i>	369
	B.4.6 <i>Visualisation Software for Surface Structures</i>	370
	<i>Appendix C Vector Calculation in Oblique Lattices</i>	371
	<i>Appendix D Distance between Neighbouring Lattice Planes in the Bravais Lattices</i>	374
	<i>Appendix E Lattice Transformations</i>	375
	E.1 <i>The (111) Surface of the fcc Lattice</i>	376
	E.2 <i>The (111) Surface of the bcc Lattice</i>	377
	E.3 <i>Hexagonal to Rhombohedral Transformation</i>	377
	E.4 <i>Rhombohedral to Hexagonal Transformation</i>	378
	<i>Appendix F Calculation of Translation Vectors for Stepped Surfaces</i>	379
	F.1 <i>Example 1</i>	380
	F.2 <i>Example 2</i>	381
	<i>Appendix G Symmetry Use in the Calculation of Reflection and Transmission Matrices</i>	383
	<i>Appendix H Symmetry Use in Tensor LEED</i>	389
	<i>Appendix I Atomic Displacement Parameters</i>	393
	I.1 <i>Isotropic Displacements and Gaussian Distributions</i>	394
	I.2 <i>Anisotropic Displacements and Gaussian Distributions</i>	394
	I.2.1 <i>Anisotropic Displacement Parameter β^{ij}</i>	395

<i>1.2.2 Anisotropic Displacement Parameter U^{ij}</i>	396
<i>1.2.3 Anisotropic Displacement Parameter in Cartesian Coordinates U_{ij}^C</i>	396
<i>1.2.4 Relation between U^{ij} and β^{ij}</i>	397
<i>1.2.5 Relation between U^{ij} and U_{ij}^C</i>	397
<i>1.2.6 Equivalent Isotropic Displacement Parameters</i>	397
<i>Appendix J Averaging over Domains</i>	399
<i>References</i>	402
<i>Index</i>	431