

Jian Min Zuo · John C.H. Spence

# Advanced Transmission Electron Microscopy

Imaging and Diffraction in Nanoscience

 Springer

# Contents

<b>1</b>	<b>Introduction and Historical Background</b> . . . . .	1
1.1	Electrons and the Electron Wavelength . . . . .	1
1.2	Electron and Sample Interaction . . . . .	2
1.3	Transmission Electron Microscope . . . . .	5
1.4	Electron Microdiffraction and STEM . . . . .	7
1.5	Analytical TEM . . . . .	9
1.6	A Brief History of Electron Microdiffraction . . . . .	12
1.7	A Note to Students and Lecturers . . . . .	16
	References . . . . .	17
<b>2</b>	<b>Electron Waves and Wave Propagation</b> . . . . .	19
2.1	Wave Functions and the Wave Equation . . . . .	19
2.2	Quantum Mechanical Wave of Electrons and Schrödinger Equation . . . . .	22
2.3	The Principle of Wave Superposition . . . . .	24
2.4	Amplitude and Phase Diagrams . . . . .	25
2.5	Coherence and Interference . . . . .	25
2.6	Wave Packets and the Uncertainty Principle . . . . .	28
2.7	The Gaussian Wave Packet and Its Propagation . . . . .	31
2.8	Temporal Coherence . . . . .	33
2.9	Spatial Coherence . . . . .	35
2.10	Electron Refraction and the Refractive Index . . . . .	38
2.11	Wave Propagation . . . . .	39
	2.11.1 Huygens–Fresnel Principle . . . . .	39
	2.11.2 Propagation of Plane Wave and Fresnel Zones . . . . .	41
	2.11.3 Fresnel Diffraction—The Near-Field Small-Angle Approximation . . . . .	43
	2.11.4 Fraunhofer Diffraction—Far-Field Forward Diffraction . . . . .	46
	References . . . . .	47

<b>3</b>	<b>The Geometry of Electron Diffraction Patterns</b> . . . . .	49
3.1	Bragg's Law . . . . .	49
3.2	Laue Diffraction Condition . . . . .	52
3.3	Lattice $d$ -Spacing and Crystal, Real, and Reciprocal Lattices . . . . .	52
3.4	Transmission Electron Diffraction Patterns . . . . .	54
3.5	Excitation Error . . . . .	56
3.6	Kikuchi Lines and Their Geometry (Kinematic) . . . . .	59
3.7	Diffraction Pattern Indexing . . . . .	64
3.8	One-Dimensional (Systematics) CBED . . . . .	65
3.9	Two-Dimensional CBED . . . . .	69
3.10	High-Order Laue Zone (HOLZ) Lines . . . . .	71
	References . . . . .	75
<b>4</b>	<b>Kinematical Theory of Electron Diffraction</b> . . . . .	77
4.1	First-Order Born Approximation . . . . .	78
4.2	Weak-Phase-Object Approximation . . . . .	80
4.3	Electron Atomic Scattering . . . . .	82
4.4	Kinematical Electron Scattering from a Monoatomic Small Crystal . . . . .	86
4.5	Electron Crystal Structure Factors and the Diffracted Intensity from a Small Crystal . . . . .	88
4.6	Integrated Diffraction Intensity of a Rotating Crystal . . . . .	90
4.7	Atomic Thermal Vibrations and Effect on Electron Scattering . . . . .	92
4.8	Electron Structure Factors . . . . .	95
4.9	Electron-Optical Potential . . . . .	97
	References . . . . .	100
<b>5</b>	<b>Dynamical Theory of Electron Diffraction for Perfect Crystals</b> . . . . .	101
5.1	Many-Beam Theory, Wave-Mechanical Approach . . . . .	102
5.2	Howie-Whelan Equations . . . . .	107
5.3	Two-Beam Theory . . . . .	109
5.4	The Concept of the Dispersion Surface . . . . .	112
5.5	Absorption and Its Effects in a First-Order Approximation . . . . .	117
5.6	Many-Beam Effects . . . . .	121
5.6.1	Three-Beam Theory and Particular Solutions for Centrosymmetric Crystals . . . . .	122
5.6.2	Two-Beam Theory with Weak-Beam Effects . . . . .	125
5.6.3	Three-Beam Theory—Noncentrosymmetric Crystals and the Phase Problem . . . . .	126
5.6.4	Dynamic HOLZ Intensities and Positions. Dispersion Surfaces for HOLZ Lines. How the Bragg Law Depends on Local Composition . . . . .	133
	References . . . . .	139

<b>6</b>	<b>Electron Optics</b> .....	143
6.1	Magnetic Lenses .....	144
6.2	Fundamental Rays and Conjugate Planes .....	149
6.3	Thin Lens .....	151
6.4	Thick Lenses .....	154
6.4.1	Glaser's Bell-Shaped Model .....	154
6.4.2	Cardinal Points and Planes .....	156
6.4.3	Lens Equation .....	158
6.4.4	Determination of Cardinal Points from the Electron Path .....	159
6.5	The Objective Lens .....	161
6.6	The Objective Prefield .....	162
	References .....	163
<b>7</b>	<b>Lens Aberrations and Aberration Correction</b> .....	165
7.1	Lens Aberrations .....	165
7.2	Aberration Coefficients .....	170
7.3	Multipole Fields and Quadrupole Focal Properties .....	178
7.4	Aberrations of Hexapole Fields .....	180
7.5	$C_s$ Correctors .....	186
	References .....	191
<b>8</b>	<b>Electron Sources</b> .....	193
8.1	Source Properties .....	193
8.2	Thermionic Emission Source .....	196
8.3	Schottky Emission Source .....	198
8.4	Cold-Field Emission Source .....	202
	References .....	205
<b>9</b>	<b>Electron Detectors</b> .....	207
9.1	Scintillator-Photomultiplier Detectors .....	207
9.2	Characteristics of Point Detectors .....	210
9.3	Characteristics of ADF Detectors .....	211
9.4	CCD Cameras .....	215
9.5	Detector Characteristics of CCD Cameras .....	218
9.6	Direct Detection Cameras .....	223
9.7	Film and Image Plates .....	225
	References .....	228
<b>10</b>	<b>Instrumentation and Experimental Techniques</b> .....	231
10.1	Electron Beam Illumination .....	232
10.1.1	Illumination Using Two Condenser Lenses .....	232
10.1.2	The Use of Condenser Minilens .....	234
10.1.3	A Third Condenser Lens and Kohler Illumination .....	235
10.1.4	Beam Current .....	236
10.1.5	Coherence and Coherent Current .....	237

10.2	Probe Formation . . . . .	241
10.3	Beam Deflectors and Scanning . . . . .	246
10.4	Electron Diffraction Techniques . . . . .	250
	10.4.1 Selected Area Electron Diffraction (SAED) . . . . .	250
	10.4.2 Nanoarea Electron Diffraction (NAED) and Nanobeam Diffraction (NBD) . . . . .	251
	10.4.3 Convergent-Beam Electron Diffraction (CBED) . . . . .	252
	10.4.4 Large-Angle Methods . . . . .	255
	10.4.5 Precession Electron Diffraction . . . . .	259
	10.4.6 Selected Area Diffraction in STEM . . . . .	261
	10.4.7 Scanning Electron Nanodiffraction . . . . .	263
10.5	Specimen Holders and Rotation . . . . .	266
10.6	Energy Filtering . . . . .	269
	10.6.1 First-Order Focusing by Magnetic Sectors . . . . .	272
	10.6.2 Energy Dispersion . . . . .	276
	10.6.3 Vertical Focusing Using Fringing Fields . . . . .	277
	10.6.4 Sector Fields, Paraxial Equations, and Second-Order Aberrations . . . . .	279
	10.6.5 In-Column Energy Filters . . . . .	282
	10.6.6 Post-Column Imaging Filters . . . . .	283
	10.6.7 Isochromaticity, Filter Acceptance, and Distortion . . . . .	285
10.7	Radiation Effects and Low-Dose Techniques . . . . .	288
	References . . . . .	292
<b>11</b>	<b>Crystal Symmetry . . . . .</b>	<b>297</b>
11.1	Symmetry Operations and Symmetry Groups . . . . .	297
11.2	Point Groups . . . . .	299
11.3	Lattice and Space Groups . . . . .	303
11.4	Symmetry Operation in Real and Reciprocal Spaces . . . . .	311
11.5	Symmetry Determination Using Kinematic Diffraction Intensities . . . . .	312
11.6	Symmetry Determination by CBED . . . . .	315
	11.6.1 Point Symmetry in Dynamic Diffraction . . . . .	317
	11.6.2 Point Group Determination by CBED . . . . .	323
11.7	Bravais Lattice Determination . . . . .	328
11.8	Space Groups . . . . .	329
11.9	Quantification of CBED Pattern Symmetry and Symmetry Mapping . . . . .	335
11.10	Symmetry and Polarization in Ferroelectric Crystals . . . . .	339
	References . . . . .	343

<b>12</b>	<b>Crystal Structure and Bonding</b> .....	347
12.1	Description of Crystal Structure .....	347
12.2	Common Structure Types .....	350
12.3	Chemical Bonding .....	357
12.3.1	Bonding of a Diatomic Molecule.....	358
12.3.2	Atomic Sizes and Electronegativity .....	360
12.3.3	Bonding in Infinite Crystals.....	361
12.3.4	Types of Bonds .....	362
12.3.5	Characteristics of Bonds .....	363
12.3.6	Charge Density as the Ground-State Property in Density Functional Theory .....	365
12.4	Experimental Measurement of Charge Density .....	366
12.4.1	X-Ray Diffraction .....	366
12.4.2	Electron Diffraction .....	368
12.4.3	Combined Electron and X-Ray Analysis .....	374
12.4.4	Multipole Expansion of Electron Density .....	374
12.5	Crystal Electron Density and Bonding .....	376
12.5.1	Covalent Bonding in Diamond Structure .....	376
12.5.2	Ionic Bonding .....	381
12.5.3	Metallic Bonding .....	388
12.5.4	Transition Metal Oxides .....	391
	References.....	398
<b>13</b>	<b>Diffuse Scattering</b> .....	403
13.1	Electron Diffuse Scattering .....	404
13.2	Thermal Diffuse Scattering .....	406
13.3	Diffuse Scattering from Small Lattice Defects .....	411
13.4	Scattering by Solid Solutions .....	418
13.5	Modulated Structures .....	425
13.6	Multiple Scattering Effects in Diffuse Scattering .....	430
	References.....	438
<b>14</b>	<b>Atomic Resolution Electron Imaging</b> .....	441
14.1	Introduction and a Brief History .....	441
14.2	Abbe's Theory of Coherent Imaging .....	443
14.3	Coherent Imaging in an Ideal Lens .....	445
14.4	Coherent Imaging in a Real Lens .....	448
14.5	Linear Imaging Theory and Contrast Transfer Function (CTF) .....	449
14.6	The Effects of Electron Energy Spread and Partial Coherence .....	455
14.7	Electron Probes for High-Resolution STEM and Analysis .....	459
14.8	Probe Size and Resolution in Bright-Field STEM .....	461
14.9	Ronchigrams .....	464
14.10	Coherence in STEM .....	472

14.11	HAADF-STEM (Z-Contrast) Imaging . . . . .	476
14.12	Aberration-Corrected STEM . . . . .	478
14.13	Three-Dimensional Imaging in STEM . . . . .	481
14.14	Channeling, Bound States, and Atomic Strings. . . . .	485
14.15	Image Simulation Using the Multislice Method . . . . .	489
	References. . . . .	496
<b>15</b>	<b>Imaging and Characterization of Crystal Defects . . . . .</b>	<b>501</b>
15.1	Overview . . . . .	501
15.2	Atomic Displacements, Strain, and Stress . . . . .	505
15.3	Diffraction Contrast Imaging . . . . .	510
	15.3.1 Column Approximation . . . . .	512
	15.3.2 Thickness Fringes and Bend Contours. . . . .	513
	15.3.3 Diffraction Contrast from Lattice Defects . . . . .	515
	15.3.4 Weak-Beam Imaging . . . . .	525
15.4	Howie-Basinski Equations and the Dynamical Theory of Electron Diffraction from Crystal Defects. . . . .	529
15.5	Defect Analysis Using LACBED, Defocused CBED, and CBIM. . . . .	533
15.6	Atomic Structure Determination of Defects from High-Resolution Electron Images . . . . .	538
	15.6.1 Atomic Structure of Dislocation Cores . . . . .	539
	15.6.2 Grain Boundaries. . . . .	546
	References. . . . .	550
<b>16</b>	<b>Strain Measurements and Mapping . . . . .</b>	<b>553</b>
16.1	Local Lattice Parameters and Strain . . . . .	553
16.2	Electron Beam-Based Strain Measurement Techniques. . . . .	555
16.3	Limitations of Electron Beam Techniques . . . . .	559
16.4	Electron Diffraction-Based Strain Measurement Techniques and Applications . . . . .	560
	16.4.1 Nanobeam Diffraction . . . . .	560
	16.4.2 Diffraction Geometry . . . . .	560
	16.4.3 Strain Mapping . . . . .	562
	16.4.4 Convergent Beam Electron Diffraction (CBED) . . . . .	565
	16.4.5 3D Strain and Deformation Gradient Matrix . . . . .	567
	16.4.6 HOLZ Line Splitting from 3D Strain. . . . .	568
16.5	Electron Imaging-Based Strain Measurement Techniques and Applications . . . . .	570
	16.5.1 Strain Mapping Using GPA. . . . .	570
	16.5.2 STEM and Its Application for Strain Measurements . . . . .	572
16.6	Off-Axis Electron Holography . . . . .	574
	References. . . . .	577

<b>17</b>	<b>Structure of Nanocrystals, Nanoparticles, and Nanotubes</b> . . . . .	<b>581</b>
17.1	Nanostructures and Nanoscale Phenomena . . . . .	581
17.2	Structure of Nanocrystals . . . . .	583
17.2.1	Nanocrystal Equilibrium and Kinetic Shapes . . . . .	583
17.2.2	Nanocrystal Facet Determination . . . . .	585
17.2.3	Identification of Planar Faults Using Coherent CBED . . . . .	591
17.2.4	Nanocrystal Surface Reconstruction . . . . .	593
17.2.5	Surface Atoms of a Twinned Nanocrystal . . . . .	600
17.2.6	The Equilibrium Shape of Supported Nanocrystals . . . . .	602
17.2.7	Triple Junctions and Line Tension . . . . .	606
17.2.8	Interaction with Surface Steps . . . . .	608
17.3	Structure of Nanoclusters and Nanoparticles . . . . .	611
17.3.1	Diffraction by Free Clusters . . . . .	611
17.3.2	Structure and Energetics of Metallic Nanoparticles . . . . .	613
17.4	Carbon Nanostructures . . . . .	618
17.4.1	Carbon Allotropes and Bond Lengths . . . . .	618
17.4.2	Electron Diffraction of Carbon Nanotubes . . . . .	622
17.4.3	Chirality and Diameters of Single-Walled Carbon Nanotubes . . . . .	627
17.4.4	Structure of Multiwalled Carbon Nanotubes . . . . .	631
17.4.5	Defects in Graphene and Carbon Nanotubes . . . . .	633
17.4.6	Van der Waals Forces and Molecular Interactions . . . . .	637
	References . . . . .	644
	<b>Appendix A: Useful Relationships in Electron Diffraction</b> . . . . .	<b>653</b>
	<b>Appendix B: Electron Wavelengths, Physical Constants, and Atomic Scattering Factors</b> . . . . .	<b>655</b>
	<b>Appendix C: Crystallographic Data</b> . . . . .	<b>667</b>
	<b>Appendix D: Indexed Diffraction Patterns with HOLZ</b> . . . . .	<b>675</b>
	<b>Appendix E: Fourier Transforms, <math>\delta</math>-Function, and Convolution</b> . . . . .	<b>685</b>
	<b>Appendix F: Crystal Structure Data, Mean Inelastic Free Path, and Mean Potential</b> . . . . .	<b>691</b>
	<b>Author Index</b> . . . . .	<b>701</b>
	<b>Subject Index</b> . . . . .	<b>717</b>