Principles of Materials Characterization and Metrology

Kannan M. Krishnan

University of Washington, Seattle



Contents

1.	Intro	oduction to Materials Characterization, Analysis, and Metrology	1		
	1.1	1.1 Microstructure, Characterization, and the Materials Engineering Tetrahedron			
	1.2	Examples of Characterization and Analysis	7		
		1.2.1 Ni-Based Superalloys: Ultrahigh Temperature Materials for Jet Engines	8		
		1.2.2 Unraveling the Structure of Deoxyribonucleic Acid (DNA)	. 10		
		1.2.3 Characterizing a Picasso Painting Reveals Hidden Secrets	12		
		1.2.4 Failure Analysis: Metallurgy of the RMS Titanic	13		
		1.2.5 Beneath Our Feet: Microstructure of Rocks and Minerals	15		
		1.2.6 Ceramic Materials: Sintering and Grain Boundary Phases	17		
		1.2.7 Microstructure and the Properties of Materials: An Engineering Example	20		
	1.3	Probes for Characterization and Analysis: An Overview	22		
		1.3.1 Probes and Signals	22		
		1.3.2 Probes Based on the Electromagnetic Spectrum and Their Attributes	22		
		1.3.3 Wave–Particle Duality	24		
		1.3.4 Nature and Propagation of Electromagnetic Waves	27		
		1.3.5 Interactions of Probes with Matter and Criteria for Technique Selection	29		
	1.4	Methods of Characterization: Spectroscopy, Diffraction, and Imaging	34		
		1.4.1 Spectroscopy: Absorption, Emission, and Transition Processes	34		
		1.4.2 Scattering and Diffraction	37		
		1.4.3 Imaging and Microscopy	41		
		1.4.4 Digital Imaging	48		
		1.4.5 In Situ Methods across Spatial and Temporal Scales	56		
	1.5	Features of Materials Used for Characterization	57		
		Summary	59		
		Further Reading	59		
		References	61		
		Exercises	63		

xii	Со	intents				
2.	Ato	omic Structure and Spectra	68			
	2.1 Introduction					
	2.2	Atomic Structure	69			
		2.2.1 Bohr-Rutherford-Sommerfeld Model	69			
		2.2.2 Quantum Mechanical Model	70			
	2.3	Atomic Spectra: Transitions, Emissions, and Secondary Processes	78			
		2.3.1 Dipole Selection Rules and Allowed Transitions of Electrons in Atoms	78			
		2.3.2 Characteristic X-Ray Emissions and their Nomenclature	85			
		2.3.3 Non-Radiative Auger Electron Emission	91			
		2.3.4 Electron Photoemission	9 7			
	2.4	X-Rays as Probes: Generation and Transmission of X-Rays	97			
		2.4.1 Laboratory Sources and Methods of X-Ray Generation	9 8			
		2.4.2 X-Ray Absorption and Filtering	102			
		2.4.3 Synchrotron Sources of X-Ray Radiation	105			
	2.5	X-Rays as Signals: Core-Level Spectroscopy with X-Rays	107			
		2.5.1 Instrumentation for Detecting X-Rays	107			
		2.5.2 Chemical X-Ray Microanalysis	113			
	2.6	Surface Analysis: Spectroscopy with Electrons	119			
		2.6.1 Instrumentation for Surface Analysis with Electron Spectroscopy	120			
		2.6.2 Auger Electron Spectroscopy	123			
		2.6.3 X-Ray Photoelectron Spectroscopy	128			
		2.6.4 Surface Compositional Analysis with AES and XPS	134			
		2.6.5 Comparison of AES and XPS	136			
	2.7	Select Applications	137			
		2.7.1 XRF Analysis of Dental and Medical Specimens	137			
		2.7.2 Environmental Science: Contamination in Ground Water Colloids	138			
		Summary	139			
		Further Reading	140			
		References	142			
		Exercises	143			
3.	Bon	ding and Spectra of Molecules and Solids	147			
	3.1	Introduction	148			
	3.2	Bonds and Bands	149			
	3.3	Interatomic Bonding in Solids	152			
		3.3.1 Ionic Bonding	153			
		3.3.2 Covalent Bonding	155			
		3.3.3 Metallic Bonding	156			

				Contents	xiii
	3.4	Molecu	lar Spectra		158
		3.4.1	Vibrational and Rotational Modes		158
		3.4.2	Ultraviolet and Visible Spectroscopy (UV-Vis)		162
		3.4.3	Classical Model of Rayleigh and Raman Scattering		166
		3.4.4	Selection Criteria for Infrared and Raman Activity		169
	3.5	Infrared	1 Spectroscopy		172
		3.5.1	Instrumentation for Raman and IR Spectroscopy		173
		3.5.2	Michelson Interferometer and the Fourier Transform Infrared (FTIR) Method		174
		3.5.3	Practice and Application of FTIR		177
	3.6	Raman	Spectroscopy		179
		3.6.1	Raman, Resonant Raman, and Fluorescence		179
		3.6.2	Instrumentation for Raman Spectroscopy and Imaging		181
		3.6.3	Application of Raman Spectroscopy in Chemical and Materials Analysis		182
		3.6.4	Surface-Enhanced Raman Spectroscopy (SERS)		183
	3.7	Probing	the Electronic Structure of Solids		185
	3.8	Photoer	nission and Inverse Photoemission from Solids		188
	3.9	Absorp	tion Spectroscopies-Probing Unoccupied States		197
		3.9.1	X-Ray Absorption Spectroscopy (XAS)		197
		3.9.2	Near-Edge and Extended X-Ray Absorption Fine Structure (NEXAFS and EXAFS)		200
	3.10	Select A	Applications		206
		3.10.1	Structure of Proteins Resolved by FTIR		206
		3.10.2	Analysis of Catalytic Particles by XAS and XPS		208
		Summa	lry .		208
		Further	Reading		211
		Referen	lices		212
		Exercis	es		214
4.	Cryst	tallograp	phy and Diffraction		220
	4.1	The Cr	ystalline State		222
		4.1.1	Lattices		223
		4.1.2	Generalized Crystal Systems and Bravais Lattices		224
		4.1.3	Lattice Points, Lines, Directions, and Planes		227
		4.1.4	Zonal Equations		231
		4.1.5	Atomic Size, Coordination, and Close Packing		233
		4.1.6	Describing Crystal Structures—Some Examples		236
		4.1.7	Symmetry and the International Tables for Crystallography		239
		4.1.8	The Stereographic Projection		244
		4.1.9	Imperfections in Crystals		247

xiv	r Ca	mtents	
	4.2	The Reciprocal Lattice	250
	4.3	Diffraction	256
		4.3.1 Bragg's Law: Interpreting Diffraction in Real Space	257
		4.3.2 The Ewald Construction: Interpreting Diffraction in Reciprocal Space	259
		4.3.3 Comparison of X-Ray and Electron Diffraction	262
	4.4	Quasicrystals and the Definition of a Crystalline Material	266
		Summary	267
		Further Reading	268
		References	269
		Exercises	270
5.	Prot	pes: Sources and Their Interactions with Matter	277
	5.1	Introduction	278
	5.2	Probes and Their Generation	278
		5.2.1 Photons: Lamps and Lasers	278
		5.2.2 Electrons: Thermionic and Field-Emission Sources	282
		5.2.3 Neutrons	287
		5.2.4 Ions	288
	5.3	Interactions of Probes with Matter, Including Damage	292
		5.3.1 Photons	293
		5.3.2 Electrons	294
		5.3.3 Neutrons	303
		5.3.4 Protons	303
		5.3.5 Ions	304
	5.4	Ion-Based Characterization Methods	315
		5.4.1 Rutherford Back-Scattering Spectroscopy (RBS)	315
		5.4.2 Low-Energy Ion Scattering Spectroscopy (LEISS)	325
		5.4.3 Secondary Ion Mass Spectrometry (SIMS)	328
		5.4.4 Induction-Coupled Plasma Mass Spectrometry (ICP-MS)	331
		5.4.5 Particle-Induced X-Ray Emission (PIXE)	336
		Summary	337
		Further Reading	338
		References	339
		Exercises	339
6.	Opti	cs, Optical Methods, and Microscopy	345
	6.1	Introduction	216
	6.2	Wave Equation for Simple Harmonic Motion	340
			540

			Contents	xv	
	6.2.1	The Phase Angle		347	
	6.2.2	The Superposition Principle		348	
	6.2.3	Phasor Representation and the Addition of Waves		350	
	6.2.4	Complex Representation of a Simple Harmonic Wave		350	
	6.2.5	Superposition of Two Waves of the Same Frequency		351	
	6.2.6	Addition of Waves on Orthogonal Planes and Polarization		353	
6.3	Huyge	ns' Principle		356	
6.4	Young	Double-Slit Experiment		357	
6.5	Reflec	tion and Refraction		359	
6.6	Diffra	ction		361	
	6.6.1	Fraunhofer Diffraction from a Single Slit		363	
	6.6.2	Fraunhofer Diffraction from Double and Multiple Slits		366	
	6.6.3	Resolving Power of a Diffraction Grating		369	
	6.6.4	Fresnel Diffraction		370	
	6.6.5	Fresnel Half-Period Zones		371	
	6.6.6	Diffraction by a Circular Aperture or Disc		372	
	6.6.7	Zone Plates and Their Applications in X-Ray Microscopy		373	
6.7	Visual	ly Observable: Characteristics of the Human Eye		375	
6.8	Optica	al Microscopy		376	
	6.8.1	Resolution: Rayleigh and Abbe Criteria		376	
	6.8.2	Geometric Optics and Aberrations		378	
	6.8.3	The Optical Microscope		381	
	6.8.4	Confocal Scanning Optical Microscopy (CSOM)		386	
	6.8.5	Metallography		388	
6.9	Ellipsometry				
	6.9.1	p- and s-Polarized Light Waves, and Fresnel Equations of Reflection		394	
	6.9.2	Optical Elements Used in Ellipsometry		397	
	6.9.3	Ellipsometry Measurements		398	
	Sumn	hary		400	
	Furth	er Reading		401	
	Refere	ences		402	
	Exerc	ses		402	
X-R	ay Diff	raction		408	
7.1	Introd	uction		409	
7.2	Interaction of X-Rays with Electrons				
	7.2.1	Thomson Coherent Scattering		410	
	7.2.2	Compton Incoherent Scattering		413	

7.

xvi	Cont	Contents					
5	7.3	Scatter	ing by an Atom: Atomic Scattering Factor	415			
5	7.4	Scatteri	ing by a Crystal: Structure Factor	422			
2	7.5	Examp	les of Structure Factor Calculations	425			
		7.5.1	Face-Centered Cubic (FCC) Structure	425			
		7.5.2	Body-Centered Cubic (BCC) Structure	427			
		7.5.3	Hexagonal Close Packed (HCP) Structure	428			
		7.5.4	Cesium Chloride (CsCl) Structure	429			
7	7.6	Symme	etry and Structure Factor	431			
		7.6.1	Crystals with Inversion Symmetry	431			
		7.6.2	Friedel Law	431			
		7.6.3	Systematic Absences	431			
7	7.7	The Inv	verse Problem of Determining Structure from Diffraction Intensities	432			
7	7.8	Broade	ning of Diffracted Beams and Reciprocal Lattice Points	433			
7	7 .9	Method	ds of X-Ray Diffraction	437			
		7.9.1	The Laue Method for Single Crystals	438			
		7.9.2	Diffractometry of Powders and Single Crystals	439			
		7.9.3	Debye-Scherrer Method for Powders	443			
		7.9.4	Thin Films and Multilayers: Diffractometry, Reflectivity, and Pole Figures	445			
		7.9.5	Practical Considerations: Collimators and Monochromators	449			
7.	10	Factors	Influencing X-Ray Diffraction Intensities	451			
		7.10.1	Temperature Factor	451			
		7.10.2	Absorption or Transmission Factor	453			
		7.10.3	Lorentz Polarization Factor	455			
		7.10.4	Multiplicity	457			
		7.10.5	Corrected Intensities for Diffractometry and the Debye-Scherrer Camera	457			
7.	11	Applica	ations of X-Ray Diffraction	459			
		7.11.1	Measurement of Lattice Parameters	460			
		7.11.2	Crystallite or Grain Size and Lattice Strain Measurements	460			
		7.11.3	Phase Identification and Structure Refinement	461			
		7.11.4	Chemical Order–Disorder Transitions	464			
		7.11.5	Short-Range Order (SRO) and Diffuse Scattering	467			
		7.11.6	In Situ X-Ray Diffraction at Synchrotrons	468			
		7.11.7	X-Ray Diffraction Measurements on Mars	469			
		Summa	ıry	471			
		Further	Reading	472			
		Referen	nces	473			
		Exercise	es	474			

			Contents	xvii
8.	Diff	raction	of Electrons and Neutrons	481
	8.1	1 Introduction		
	8.2	The A	tomic Scattering Factor for Electrons	482
	8.3	Basics	of Electron Diffraction from Surfaces	485
		8.3.1	Surface Reconstruction, Surface Nets, and Their Notation	486
		8.3.2	Reciprocal Lattice Nets and Ewald Sphere Construction in Two Dimensions	487
	8.4	Surfac	ce Electron Diffraction Methods and Applications	489
		8.4.1	Low-Energy Electron Diffraction (LEED)	490
		8.4.2	Adsorption Studies on Surfaces Using LEED	493
		8.4.3	Reflection High-Energy Electron Diffraction (RHEED)	494
		8.4.4	RHEED Oscillations: In Situ Monitoring of Thin Film Growth	498
	8.5	Trans	mission High-Energy Electron Diffraction	501
		8.5.1	Coherent, Incoherent, Elastic, and Inelastic Scattering	504
		8.5.2	Basics of Electron Diffraction in a Transmission Electron Microscope	505
		8.5.3	Kinematical Theory of Electron Diffraction	506
		8.5.4	The Column Approximation, Dynamical Diffraction, and Diffraction from Imperfect Crystals	509
	8.6	Trans	mission Electron Diffraction Methods	514
		8.6.1	Selected Area Diffraction: Ring and Spot Patterns	514
		8.6.2	Kikuchi Lines, Maps, and Patterns	519
		8.6.3	Convergent Beam Electron Diffraction (CBED)	523
	8.7	Exam	ples of Transmission Electron Diffraction of Materials	527
		8.7.1	Indexing a Single Crystal Diffraction Pattern	527
		8.7.2	Polycrystalline Materials and Nanoparticle Arrays	527
		8.7.3	Orientation Relationships Between Crystals or Phases	529
		8.7.4	Chemical Order in Materials	529
		8.7.5	Diffraction from Long-Period Multilayers	531
		8.7.6	Twinning	532
	8.8	Intera	ctions of Neutrons with Matter	535
		8.8.1	Nuclear Interactions	535
		8.8.2	Magnetic Interactions	537
		8.8.3	In Situ Kinetic Studies Using Neutrons: Hydration of Cement	538
	Summary			540
		Furth	er Reading	542
		Refere	ences	543
		Exerc	ises	544

xv	iii (Contents					
9.	Tra	insmissio	on and Analytical Electron Microscopy	552			
	9.1	1 Introduction					
	9.2 Elements and Operations of a Transmission Electron Microscope						
		9.2.1	Electron Sources: Thermionic, Field, and Schottky Emission	558			
		9.2.2	Electromagnetic Lenses	560			
		9.2.3	The Illumination Section	565			
		9.2.4	The Imaging Section: Objective Lens and Aperture	568			
		9.2.5	Specimen Handling and Manipulation	570			
		9.2.6	The Magnification Section	571			
		9.2.7	Imaging and Diffraction Modes	573			
		9.2.8	Scanning Transmission Mode and the Principle of Reciprocity	584			
		9.2.9	Correction of Lens Aberrations	587			
		9.2.10	Image Recording and Detection of Electrons	588			
	9.3	Beam-	Solid Interactions, Contrast Mechanisms, and Imaging Methods	588			
		9.3.1	Elastic Interactions	589			
		9.3.2	Mass-Thickness Contrast	592			
		9.3.3	Diffraction Contrast	5 9 5			
		9.3.4	High-Angle Incoherent Scattering: Z-Contrast Imaging	598			
		9.3.5	High-Resolution Electron Microscopy (HREM): Phase Contrast Imaging in Practice	601			
		9.3.6	Magnetic Contrast: Lorentz Microscopy	609			
		9.3.7	Electron Holography	613			
	9.4	Analyti	cal Electron Microscopy (AEM) and Related Spectroscopies	617			
		9.4.1	Inelastic Scattering and Spectroscopy	619			
		9.4.2	Electron Energy-Loss Spectroscopy (EELS) in a TEM	623			
		9.4.3	Quantitative Microanalysis with Energy-Dispersive X-Ray Spectrometry	641			
		9.4.4	Microdiffraction	648			
	9.5	Select A	Applications of TEM	650			
		9.5.1	Electron Tomography	650			
		9.5.2	Analysis of Defects: Dislocations and Stacking Faults	655			
		9.5.3	Thin Films and Multilayers: An Example	658			
		9.5.4	TEM in Semiconductor Manufacturing: Metrology, Process Development, and Failure Analysis	660			
		9.5.5	Dynamic Measurements in a TEM	664			
	9.6	Prepara	tion of Specimens for TEM Observations	666			
		9.6.1	Chemical and Electrochemical Polishing	668			
		9.6.2	Ion-Beam Milling	669			
		9.6.3	Ultramicrotomy and Preparation of Biological Materials	669			
		9.6.4	Preparation of Cross-Section Specimens	669			
		9.6.5	Focused Ion-Beam (FIB) Milling	670			

			Contents	xix
		Summary		671
		Further Reading		674
		References		675
		Exercises		684
10	Scan	aing Flectron Microscony		693
10.	10.1	Introduction		604
	10.1	The Scorping Plastran Microscorp		694
	10.2	10.2.1 The Instrument		601
		10.2.1 The Instrument		694
		10.2.2 The Evernari–Thorniey Electron Detector		600
		10.2.4 The Insident Darks Size and Sugars		701
		10.2.4 The incident Probe Size and Spatial Resolution		701
		10.2.5 Depth of Field		705
		10.2.5 Noise and Contrast in Imaging		700
		10.2.7 Elastic and Inelastic Scattering, and Beam Broadening		707
	10.3	Image Contrast in a Scanning Electron Microscope		709
		10.3.1 Factors Influencing Secondary Electron Emission		710
		10.3.2 Topographical Contrast in Secondary Electron Imaging		715
		10.3.3 Angular Dependence of Back-Scattered Electrons and Topographic Information		715
		10.3.4 Comparison of SEM Images with Different Operating Parameters		/18
	10.4	Channeling and Electron Back-Scattered Diffraction Patterns (EBSD)		720
	10.5	Imaging Magnetic Domains		722
		10.5.1 Type I and Type II Magnetic Contrast		/22
		10.5.2 Scanning Electron Microscopy with Polarization Analysis (SEMPA)		723
	10.6	Probing Sample Composition and Electronic Structure		/26
		10.6.1 Basics of X-Ray Microanalysis in an SEM		726
		10.6.2 Cathodoluminescence		731
	10.7	Variations of Scanning Electron Microscopy		/32
		10.7.1 Environmental Scanning Electron Microscopy (ESEM)		732
		10.7.2 Combined Focused Ion-Beam (FIB) and Scanning Electron Microscope		734
	10.8	Preparing Specimens for SEM		736
		Summary		737
		Further Reading		738
		References		739
		Exercises		/40
11.	Scan	ning Probe Microscopy		745
	11.1	Introduction		746
	11.2	Physics of Scanning Tunneling Microscopy (STM)		749

xx Contents

		11.2.1	Elastic Tunneling Through a One-Dimensional Barrier	749		
		11.2.2	Quantum Mechanical Tunneling Model of the STM	750		
	11.3	Basic C	Dperation of the Scanning Tunneling Microscope	752		
		11.3.1	Imaging	753		
		11.3.2	Tunneling Spectroscopy	755		
		11.3.3	Manipulation of Adsorbed Atoms on Clean Surfaces	757		
	11.4	Physics	of Scanning Force Microscopy	759		
		11.4.1	Mechanical Characteristics of the Cantilever	760		
		11.4.2	Cantilever as a Force Sensor	763		
		11.4.3	Tip-Specimen Forces Encountered in an SFM	765		
	11.5	Operati	ion of the Scanning Force Microscope	767		
		11.5.1	Static Contact Mode for Topographic Imaging	769		
		11.5.2	Lateral Force Microscopy	772		
		11.5.3	Dynamic Noncontact Modes of Atomic Force Microscopy	773		
	11.6	Scannii	ng Force Microscopy Instrumentation	776		
	11.7	Artifact	ts in Scanning Probe Microscopy	777		
		11.7.1	Probe Artifacts	777		
		11.7.2	Instrument Artifacts	780		
	11.8	Select A	Applications of Scanning Force Microscopy	780		
		11.8.1	Atomic Fingerprinting in Frequency Modulated Atomic Force Microscopy	781		
		11.8.2	Magnetic Force Microscopy (MFM)	782		
		11.8.3	Scanning Thermal Microscopy (SThM)	785		
		11.8.4	Applications of Atomic Force Microscopy in the Life Sciences	786		
		11.8.5	Dip-Pen Nanolithography (DPN)	793		
		Summa	ry .	794		
		Further	Reading	795		
		Referen	nces	796		
		Exercise	es	799		
12.	Sumr	nary Ta	bles	803		
	Table	12.1 S	pectroscopy and Chemical Methods	804		
	Table	12.2 D	Diffraction and Scattering Methods	814		
	Table	12.3 Ir	naging Methods	818		
	Index					
	Table of values					
	Periodic Table of the Elements					