

*Reflection electron microscopy  
and spectroscopy for  
surface analysis*

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**CAMBRIDGE**  
UNIVERSITY PRESS

## *Preface*

This book was written following my review article 'Electron reflection, diffraction and imaging of bulk crystal surfaces in TEM and STEM', published by *Reports on Progress in Physics* [56 (1993) 997]. Thanks are due to Dr Simon Capelin, the Editorial Manager of Cambridge University Press, for inviting me to write this book. The book is intended for surface scientists and microscopists who are interested in surface characterizations using reflected electron diffraction and imaging techniques.

Many of the ideas illustrated in the book were collected from my past working experiences with Professor J. M. Cowley, Dr J. Bentley, Professor R. F. Egerton, Dr Ping Lu and Dr J. Liu, to whom I am very grateful. Thanks also go to Professor J. C. H. Spence for his initial suggestions when this book was proposed. I heartily thank Dr Nea Wheeler for her careful and critical reviewing of the manuscript, which significantly improved its quality.

I am grateful to Drs C. C. Ahn, H. Banzhof, E. Bauer, P. A. Crozier, R. Garcia-Molina, J. M. Gibson, H. Homma, T. Hsu, A. Ichimiya, S. Ino, M. Iwatsuki, A. V. Latyshev, G. Lehmppfuhl, J. Liu, L. V. Litvin, H. Marten, G. Meyer-Ehmsen, H. Nakahara, H. Nakayama, N. Osakabe, J. C. H. Spence, Y. Tanishiro, K. Yagi, Y. Yamamoto and N. Yao, for permission to use their micrographs to illustrate the text. Thanks also go to Drs T. Hsu and L. M. Peng, who kindly provided the original REM bibliography text file.

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# *Symbols and definitions*

Listed below are some of the symbols frequently used in this book. All quantities are defined in SI units.

$h$	Planck's constant
$\hbar$	$= h/2\pi$
$c$	The speed of light in a vacuum
$m_0$	The rest mass of an electron
$m_e$	The mass of an electron with relativistic correction
$e$	The absolute charge of an electron
$k_B$	Boltzmann's constant
$U_0$	The accelerating voltage of an electron microscope
$\lambda$	The electron wavelength in free space
$p$	The momentum of an incident electron
$K_0$	The wavevector of an incident electron beam, $K_0 = 1/\lambda$
$K$	The wavevector of a diffracted electron beam, $K = 1/\lambda$
$\omega$	Frequency
$\vartheta$	The electron scattering semi-angle
$f_\gamma^e$	The electron scattering factor of the $\alpha$ th atom
$f_\gamma^x$	The X-ray scattering factor of the $\alpha$ th atom
$\kappa$	The $\kappa$ th atom in a crystal
$\sum_\kappa$	Sum over all atoms in crystal
$\sum_\tau$	Sum over atoms within the unit cell
FT	Fourier transform from real space to reciprocal space
FT <sup>-1</sup>	Inverse Fourier transform
$r$	$= (x, y, z)$ . A real-space vector
$b$	$= (x, y)$ . A real-space vector
$g$ (or $h$ )	A reciprocal-lattice vector
$u$ (or $\tau$ )	A reciprocal-space vector
$V(r)$	The electrostatic potential distribution in a crystal
$V(u)$	$= \text{FT}(V(r))$ . The kinematic scattering amplitude of the crystal

# SYMBOLS AND DEFINITIONS

$V_{\kappa}(\mathbf{r})$	The electrostatic potential of the $\kappa$ th atom
$\rho_{\kappa}(\mathbf{r})$	The electron density distribution of the $\kappa$ th atom
$s$	The scattering vector, $s = \mathbf{u}/2$ , $s = (\sin \theta)/\lambda$
$Z$	Atomic number
$S_p$	The shape function of the crystal
$V_g$	The Fourier coefficient of the crystal potential
$V_z(\mathbf{g})$	The Fourier transform of the $z$ th atom in the unit cell
$\exp(-W_z)$	The Debye-Waller factor of the $z$ th atom
$\Omega$	The volume of a unit cell
$\mathbf{r}_z$	$= \mathbf{r}(z)$ . The position of the $z$ th atom within the unit cell
$\mathbf{R}_n$	The position vector of the $n$ th unit cell
$\mathbf{a}, \mathbf{b}, \mathbf{c}$	Base vectors of the unit cell
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$	Base vectors of the reciprocal lattice vector
$\theta_g$	The Bragg angle
$d_g$	The interplanar distance
$t$	Time
$\otimes$	Convolution
$T_{\text{obj}}(\mathbf{u})$	The transfer function of the objective lens in reciprocal space
$A_{\text{obj}}(\mathbf{u})$	The shape function of the objective aperture in reciprocal space
$C_s$	The spherical aberration coefficient of the objective lens
$\Delta f$	The defocus of the objective lens
$\Delta f_c$	The focus shift introduced by chromatic aberration effects
$\Delta f_s$	The Schertzer defocus
$C_c$	The chromatic aberration coefficient of the objective lens
$\Delta E$	Electron energy loss
$\mathbf{A}$ and $\mathbf{B}$	Basis vectors of the crystal lattice at the surface plane
$\mathbf{A}_s$ and $\mathbf{B}_s$	Basis vectors of the surface lattice
$\mathbf{A}_s^*$ and $\mathbf{B}_s^*$	Reciprocal-lattice vectors of the surface lattice
$V_s$	The surface potential
$N_s$	The number of surface unit cells
$N_i$	The number of surface islands
$H$	Step height
$L$	The width of a surface terrace
$\langle \rangle_c$	The configurational average over atom arrangements on a surface
$\psi$	Surface coverage

## SYMBOLS AND DEFINITIONS

$\gamma$	$= [1 - (v/c)^2]^{-1/2}$ . The relativistic correction factor
$E$ (or $E_0$ )	$= eU_0[1 + eU_0/(2m_0c^2)]$ . The energy of an incident electron
$w$	$= E + m_0c^2$ . The total energy of an incident electron
$U(\mathbf{r})$	$= (2\pi m_0 e/\hbar^2)V(\mathbf{r})$ , modified crystal potential
$U_g$	The Fourier coefficient of the modified potential $U$
$v$	The velocity of an incident electron
$\Psi(\mathbf{r})$	The electron wave function
$\Phi(\mathbf{r})$	The electron wave function excluding $\exp(2\pi i \mathbf{K} \cdot \mathbf{r})$ factor, $\Phi(\mathbf{r}) = \Psi(\mathbf{r}) \exp(-2\pi i \mathbf{K} \cdot \mathbf{r})$
$B_i(\mathbf{r})$	The $i$ th branch Bloch wave
$\mathbf{k}^{(i)}$	The wavevector of the $i$ th Bloch wave
$\alpha_i$	Superposition coefficients of Bloch waves
$\mathbf{r}_x$	The position of an atom in the unit cell
$\mathbf{C}_g^{(i)}$	The eigenvector of the $i$ th Bloch wave
$v_i$	The eigenvalue of the $i$ th Bloch wave
$S_g$	Excitation error
$\xi_g$	Two-beam extinction distance
$\mathbf{R}(\mathbf{r})$	The static displacement vector of atoms in an imperfect crystal
$\mathbf{b}_B$	Burgers vectors of dislocations
$\sigma$	$= \frac{\pi e^2}{\lambda E} = \frac{1}{\hbar v}$
$\Delta z$	The thickness of a crystal slice
$\mathbf{K}_b$	The component of a wavevector in the $\mathbf{b}$ plane
$\theta$	The beam's incident angle with respect to the crystal surface
$\phi$	The beam's deviation angle parallel to the surface with respect to the zone axis
$P(\mathbf{b}, \Delta z)$	The propagation function of a slice with thickness $\Delta z$
$Q$	The phase grating function of a slice with thickness $\Delta z$
$d$	The width of the incident beam in a perpendicular-to-surface multislice calculation
$G(\mathbf{r}, \mathbf{r}')$	Green's function
$\bar{V}_0$	Average crystal inner potential
$\omega$	Angular frequency
$E_k$	Electron kinetic energy
$n_i$	The electron refraction index at the crystal surface
$B$	The incident beam's azimuth
$\vartheta_E$	The characteristic angle of inelastic scattering
$F$	The foreshortening factor

## SYMBOLS AND DEFINITIONS

$\alpha_{\text{mis}}$	The surface mis-cut angle
$\mathbf{M}_1$	The rotation matrix
$\phi_p$	The phase jump at a surface step
$D_p$	The electron penetration depth into the surface
$X_c$	The coherence distance
$d_r$	Image resolution
$\alpha$	$= \theta/2$ , semi-angle of the objective aperture
$D_f$	Depth of field
$D_i$	Depth of focus
$d_0$	Thickness of crystal foil
$a_n$	Crystal states
$\mathbf{q}$ (or $\mathbf{Q}$ )	Change in crystal wavevector
$S(\tau, \tau')$	Mixed dynamic form factor
$\tau$	Reciprocal space vector
$\rho_{n0}(\mathbf{u})$	Charge density matrix
$\Lambda$	Mean-free-path length of inelastic electron scattering
$\mathbf{R}_n$	$= \mathbf{R}(n)$ , the position of the $n$ th unit cell
$\mathbf{u}_x^{(n)}$	The vibrational displacement of $x$ th atom inside the $n$ th unit cell
$\mathbf{r}(x)$	Equilibrium position of the atom in the unit cell
$\mathbf{u}_\kappa$	The time-dependent displacement vector of the $\kappa$ th atom
$M_x$	The mass of the $x$ th atom in the unit cell
$\varepsilon$	The polarization vector of the phonon mode
$a^\dagger_j(\mathbf{q})$	Creation operators of a phonon with wavevector $\mathbf{q}$ and dispersion surface $\omega_j$
$a_j(\mathbf{q})$	The annihilation operator of a phonon with wavevector $\mathbf{q}$ and dispersion surface $\omega_j$
$V_x$	The time-dependent potential of the $x$ th atom in the unit cell
$V_{0x}$	The time-averaged atomic potential
$\Delta V$	$= V - V_0$ , perturbation of crystal potential due to atomic thermal vibration
$N_0$	The number of primitive cells in a crystal
$n_0$	The number of atoms in the primitive cell
$\omega_i$	The phonon frequency
$\langle n_s \rangle$	The average occupation number of phonon state $ n_s\rangle$
$q_m$	The radius of the Brillouin zone
$V_{\text{BZ}}$	The volume of the Brillouin zone
$T$	Temperature
$T_D$	The Debye temperature

## SYMBOLS AND DEFINITIONS

$\overline{a_k^2}$	The mean square vibration amplitude of the $k$ th atom
$v_j$	The phonon velocity
$S_{\text{TDS}}(\mathbf{Q}, \mathbf{Q}')$	The scattering function in TDS
$\epsilon(\omega, \mathbf{q})$	The dielectric function of a solid
$\frac{d^2 P}{dz d\omega}$	The differential excitation probability of valence states
$\epsilon_{\text{tr}}(\omega)$	The generalized dielectric function
$q_c$	The cut-off value of a wavevector
$\omega_p$	The resonance frequency of the volume plasmon
$\omega_s$	The resonance frequency of the surface plasmon
$\bar{m}$	The average number of plasmons excited
$\mathbf{E}(\mathbf{r}, t)$	The electric field vector
$\mathbf{B}(\mathbf{r}, t)$	The magnetic field vector
$\mathbf{J}(\mathbf{r}, t)$	The electron current density
$\rho(\mathbf{r}, t)$	The electron charge density
$\Pi$	The Hertz vector
$H'(\mathbf{r})$	The interaction Hamiltonian
$\sigma_{\text{eff}}$	The ionization cross-section of the $n$ th state
$\sigma_t$	The total ionization cross-section
$f_{\text{E}}$	The electron single inelastic scattering function
$J(R, E_0 - \Delta E)$	The electron energy-loss distribution function
$m_v$	The average number of volume plasmons excited
$m_s$	The average number of surface plasmons excited
$L_s$	The average distance that an electron travels along the surface
$\lambda$	The inelastic mean free path length
$\sigma_{\text{I}}$	The angular integrated ionization cross-section
$\Theta$	Solid angle
$\mathfrak{R}$	The Rydberg energy
$a_B$	The Bohr radius
$\beta$	The collection semi-angle of an EELS spectrometer
$\Delta$	The energy width of an integration window
$n_A$	The atom concentration
$\sigma_{\text{eff}}$	The effective angular integrated ionization cross-section
$i_A$	The channeling current density at atom sites
$n_x$	The X-ray refraction index

$\theta_c$  The critical angle for total external X-ray reflection

*Sign conventions*

Free-space plane wave  $\exp(2\pi i \mathbf{K} \cdot \mathbf{r} - i \omega t)$

Fourier transforms

real space to reciprocal space  $f(\mathbf{u}) = \int d\mathbf{r} \exp(-2\pi i \mathbf{u} \cdot \mathbf{r}) f(\mathbf{r}) \equiv \text{FT}[f(\mathbf{r})]$ ,

reciprocal space to real space  $f(\mathbf{r}) = \int d\mathbf{u} \exp(2\pi i \mathbf{u} \cdot \mathbf{r}) f(\mathbf{u}) \equiv \text{FT}^{-1}[f(\mathbf{u})]$ ,

where the limits of integration are  $(-\infty, \infty)$  unless otherwise specified.



# Contents

	<i>Preface</i>	page xiii
	<b>Symbols and definitions</b>	xiv
0	<i>Introduction</i>	1
0.1	Historical background	4
0.2	The scope of the book	6
<b>1</b>	<b>Kinematical electron diffraction</b>	9
1.1	Electron wavelength	9
1.2	Plane wave representation of an incident electron	10
1.3	The Born approximation and single-atom scattering	11
1.4	The Fourier transform	12
1.5	The scattering factor and the charge density function	13
1.6	Single-scattering theory	15
1.7	Reciprocal space and the reciprocal-lattice vector	19
1.8	Bragg's law and the Ewald sphere	20
1.9	Abbe's imaging theory	23
1.10	The phase object approximation	26
1.11	Aberration and the contrast transfer function	27
<b>Part A</b>	<b>Diffraction of reflected electrons</b>	29
<b>2</b>	<b>Reflection high-energy electron diffraction</b>	31
2.1	The geometry of RHEED	31
2.2	Surface crystallography	35
2.2.1	Surface reconstruction	36
2.2.2	Two-dimensional reciprocal space	40
2.3	Streaks and Laue rings in RHEED	41
2.4	Determination of surface structures	42
2.5	RHEED oscillation and its application in MBE crystal growth	46
2.6	The kinematical diffraction theory of RHEED	51
2.6.1	Perfectly ordered surfaces	51
2.6.2	Completely disordered surfaces	52
2.6.3	Surfaces with islands	52
2.6.4	Stepped surfaces	53
2.6.5	Surfaces with randomly distributed coverage	54
2.7	Kikuchi patterns in RHEED	55

## CONTENTS

<b>3</b>	<b>Dynamical theories of RHEED</b>	<b>60</b>
3.1	The Bloch wave theory	62
3.2	Parallel-to-surface multislice theories I	68
3.3	Parallel-to-surface multislice theories II	73
3.4	Perpendicular-to-surface multislice theory	78
3.4.1	Multislice solution of the Schrödinger equation for transmission electron diffraction	80
3.4.2	Applications in RHEED calculations	82
3.5	Diffraction of disordered and stepped surfaces	85
3.5.1	A perturbation theory	85
3.5.2	Stepped surfaces	87
<b>4</b>	<b>Resonance reflections in RHEED</b>	<b>89</b>
4.1	The phenomenon	89
4.2	The resonance parabola and the resonance condition	93
4.3	The width of the resonance parabola	95
4.4	The Kikuchi envelope	99
4.5	Dynamical calculations of resonance scattering	102
4.5.1	Low-incidence-angle resonance	104
4.5.2	High-incidence-angle resonance	107
4.5.3	Resonance at a stepped surface	109
4.5.4	A steady state wave at a surface	116
4.6	The effect of valence excitation in resonance reflection	118
4.6.1	A simplified theory	118
4.6.2	The effect on surface resonance	120
4.7	Enhancement of inelastic scattering signals under the resonance condition	126
<b>Part B</b>	<b>Imaging of reflected electrons</b>	<b>129</b>
<b>5</b>	<b>Imaging surfaces in TEM</b>	<b>131</b>
5.1	Techniques for studying surfaces in TEM	131
5.1.1	Imaging using surface-layer reflections	131
5.1.2	Surface profile imaging	134
5.1.3	REM of bulk crystal surfaces	134
5.2	Surface preparation techniques	137
5.2.1	Natural or as-grown surfaces	138
5.2.2	Re-crystallization from melting	139
5.2.3	Annealing polished surfaces	139
5.2.4	Cleaving bulk crystals	140
5.3	Experimental techniques of REM	141
5.3.1	Mounting specimens	141
5.3.2	Microscope pre-alignment	142
5.3.3	Forming REM images	143
5.3.4	Diffraction conditions for REM imaging	145
5.3.5	Image recording techniques	148

5.4	Foreshortening effects	149
5.5	Surface refraction effects	151
5.6	Mirror images in REM	155
5.7	The surface mis-cut angle and step height	156
5.8	Determining surface orientations	160
5.9	Determining step directions	161
<b>6</b>	<b>Contrast mechanisms of reflected electron imaging</b>	166
6.1	Phase contrast	166
6.2	Diffraction contrast	171
6.3	Spatial incoherence in REM imaging	177
6.4	Source coherence and surface sensitivity	180
6.5	The effect of energy filtering	182
6.6	Determining the nature of surface steps and dislocations	184
6.6.1	Step height	184
6.6.2	Down and up steps	186
6.7	REM image resolution	186
6.8	High-resolution REM and Fourier imaging	189
6.8.1	Imaging a reconstructed layer	189
6.8.2	Fourier images	190
6.9	Depth of field and depth of focus	193
6.10	Double images of surface steps	194
6.11	Surface contamination	198
<b>7</b>	<b>Applications of UHV REM</b>	199
7.1	UHV microscopes and specimen cleaning	199
7.2	<i>In situ</i> reconstruction on clean surfaces	201
7.3	Surface atom deposition and nucleation processes	203
7.4	Surface-gas reactions	206
7.5	Surface electromigration	207
7.6	Surface ion bombardment	209
7.7	Surface activation energy	210
<b>8</b>	<b>Applications of non-UHV REM</b>	211
8.1	Steps and dislocations on metal surfaces	211
8.2	Steps on semiconductor surfaces	211
8.3	Ceramics surfaces	213
8.4	<i>In situ</i> dynamic processes on ceramics surfaces	220
8.5	Surface atomic termination and radiation damage	228
8.6	Reconstruction of ceramic surfaces	232
8.7	Imaging planar defects	232
8.8	As-grown and polished surfaces	235
<b>Part C</b>	<b>Inelastic scattering and spectrometry of reflected electrons</b>	241
<b>9</b>	<b>Phonon scattering in RHEED</b>	243
9.1	Inelastic excitations in crystals	243

## CONTENTS

9.2	Phonon excitation	246
9.2.1	Phonons	246
9.2.2	The effect of atomic vibrations on the crystal potential	248
9.2.3	Electron-phonon interactions	249
9.3	The 'frozen' lattice model	251
9.4	Calculation of the Debye-Waller factor	253
9.5	Kinematical TDS in RHEED	254
9.6	Dynamical TDS in RHEED	257
9.6.1	The reciprocity theorem	259
9.6.2	The Fourier transform of Green's function	261
9.6.3	Green's function theory	262
9.6.4	A modified parallel-to-surface multislice theory	267
<b>10</b>	<b>Valence excitation in RHEED</b>	<b>270</b>
10.1	EELS spectra of bulk crystal surfaces	270
10.2	The dielectric response theory of valence excitations	272
10.3	Interface and surface excitations	275
10.3.1	Classical energy-loss theory	275
10.3.2	Localization effects in surface excitation	279
10.4	The average number of plasmon excitations in RHEED	282
10.5	Excitation of a sandwich layer	283
10.6	The dielectric response theory with relativistic correction	286
10.6.1	Maxwell's equations	286
10.6.2	Valence excitation near an interface	287
10.6.3	The transverse force on an incident electron	291
10.6.4	Calculation of REELS spectra	292
10.7	The quantum theory of valence excitation	294
10.7.1	The quantum mechanical basis of the classical theory	295
10.7.2	The density operator and dielectric response theory	298
10.8	Determination of surface phases	299
10.9	Multiple-scattering effects	303
10.9.1	Poisson's distribution law	304
10.9.2	Measurement of electron penetration depth	306
10.9.3	Measurement of electron mean traveling distance along a surface	309
<b>11</b>	<b>Atomic inner shell excitations in RHEED</b>	<b>311</b>
11.1	Excitation of atomic inner shell electrons	311
11.2	Atomic inner shell excitation in reflection mode	312
11.3	Surface ELNES	314
11.4	Surface EXELFS	316
11.5	Surface chemical microanalysis	319
11.6	The effect of strong Bragg beams	324
11.7	Resonance and channeling effects	326
11.8	Effective ionization cross-sections	328
11.9	Impurity segregation at surfaces	330
11.10	Oxygen adsorption on surfaces	331
11.11	REELS in MBE	334

<b>12</b>	<b>Novel techniques associated with reflection electron imaging</b>	<b>337</b>
12.1	Scanning reflection electron microscopy	337
12.1.1	Imaging surface steps	337
12.1.2	Imaging dislocations	341
12.2	Secondary electron imaging of surfaces	341
12.3	EDS in RHEED geometry	346
12.4	Electron holography of surfaces	346
12.4.1	Principles and theory	347
12.4.2	Surface holography	349
12.5	REM with STM	352
12.5.1	Atomic-resolution surface imaging	353
12.5.2	Artifacts in STM imaging	354
12.6	Time-resolved REM and REM with PEEM	355
12.7	Total-reflection X-ray spectroscopy in RHEED	356
12.8	Surface wave excitation Auger electron spectroscopy	361
12.9	LEED and LEEM	363
<i>Appendix A</i>	Physical constants, electron wavelengths and wave numbers	367
<i>Appendix B</i>	The crystal inner potential and electron scattering factor	369
<i>Appendix C.1</i>	Crystallographic structure systems	374
<i>Appendix C.2</i>	A FORTRAN program for calculating crystallographic data	378
<i>Appendix D</i>	Electron diffraction patterns of several types of crystal structures	382
<i>Appendix E.1</i>	A FORTRAN program for single-loss spectra of a thin crystal slab in TEM	386
<i>Appendix E.2</i>	A FORTRAN program for single-loss REELS spectra in RHEED	390
<i>Appendix E.3</i>	A FORTRAN program for single-loss spectra of parallel-to-surface incident beams	393
<i>Appendix E.4</i>	A FORTRAN program for single-loss spectra of interface excitation in TEM	398
<i>Appendix F</i>	A bibliography of REM, SREM and REELS	403
<b>References</b>		<b>419</b>
<b>Materials index</b>		<b>431</b>
<b>Subject index</b>		<b>433</b>

# *Introduction*

In 1986, E. Ruska was awarded the Nobel Physics Prize for his pioneering work of building the world's first transmission electron microscope (TEM) in the late 1920s. The mechanism of TEM was originally based on the physical principle that a charged particle could be focused by magnetic lenses, so that a 'magnifier' similar to an optic microscope could be built. The discovery of wave properties of electrons really revolutionized people's understanding about the potential applications of a TEM. In the last 60 years TEM has experienced a revolutionary development both in theory and in electron optics, and has become one of the key research tools for materials characterization (Hirsch *et al.*, 1977; Buseck *et al.*, 1989). The point-to-point image resolution currently available in TEM is better than 0.2 nm, which is comparable to the interatomic distances in solids.

High-resolution TEM is one of the key techniques for real-space imaging of defect structures in crystalline materials. Quantitative structure determination is becoming feasible, particularly with the following technical advances. The installation of an energy-filtering system on a TEM has made it possible to form images and diffraction patterns using electrons with different energy losses. Accurate structure analysis is possible using purely elastically scattered electrons, scattering of which can be exactly simulated using the available theories. The traditional method of recording images on film is being replaced by digital imaging with the use of a charge-coupled device (CCD) camera, which has a large dynamical range with single-electron detection sensitivity. Thus, electron diffraction patterns and images can be recorded linearly in intensity, and a quantitative fitting is feasible between an experimentally observed image and a theoretically simulated image. This is the future direction of electron microscopy, which allows quantitative structure determination with an accuracy comparable to that of X-ray diffraction. A modern TEM is a versatile machine, which can not only explore the crystal structure using imaging and diffraction techniques but also can perform high-spatial resolution microanalysis using energy-dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). Thus the chemical composition in a region of diameter smaller than a few nanometers can be determined. Therefore, TEM is usually known as high-resolution analytical electron microscopy, which is becoming an indispensable technique for materials research.

A wide variety of diffraction, spectroscopy, and microscopy techniques are now

## INTRODUCTION

available for the characterization of thin films and surfaces; but only the microscope methods, primarily those using electrons, are able to provide direct real-space information about local inhomogeneities. Accompanying the extended applications in materials science and thin crystal characterizations, TEM has been employed to image the surface structure. There are several techniques, such as weak-beam dark-field and surface profile imaging techniques (Cowley, 1986; Smith, 1987), that have been developed for studying surface structures in TEM. This book is about reflection high-energy electron diffraction (RHEED), reflection electron microscopy (REM), scanning REM (SREM) and the associated analytical techniques for studying bulk crystal surfaces and surfaces deposited with thin films. Emphasis is placed on real-space imaging of surface structures at high resolution. These techniques can be applied to perform *in situ* studies of surfaces prepared in the molecular beam epitaxy (MBE) chamber.

A surface is a special state of condensed matter, and it is the boundary between materials and a vacuum. In the semiconductor device industry, for example, techniques are needed to control surface structures in order to control some specific transport properties. Epitaxial growth of thin films is becoming an indispensable technique for synthesizing new materials, such as superconductor thin films, semiconductor superlattices, metallic superlattices (or multilayers) and diamond films, which have important applications in advanced technologies. Therefore, surface characterization is an essential branch of materials science.

Techniques that have been applied to investigate surface structures are classified into the following categories: surface crystallography, diffraction and imaging, electron spectroscopy, incident ion techniques, desorption spectroscopy, tunneling microscopy, work function techniques, atomic and molecular beam scattering, and vibration spectroscopy. An introduction to these techniques has been given by Woodruff and Delchar (1994). Table 0.1 compares various imaging and diffraction techniques that have been developed for surface studies. Each of these techniques has its unique advantages, and most of the techniques use an electron beam as the probe. As limited by the physical mechanisms and the equipment designs, however, most of these techniques may not be adequate to be applied for imaging *in situ* surface phenomena. In this book, we introduce the reflection high-energy electron diffraction (RHEED) and reflection electron microscopy and spectrometry techniques, which can be applied to *in situ* observations of thin film nucleation and growth.

For surface studies it is rarely satisfactory to use only one technique. Information regarding structure, composition and electronic structure is usually required in order to accurately determine the surface structure. Therefore, imaging techniques are usually applied in conjunction with other techniques that can provide surface-sensitive chemical and electronic structures. The two most commonly used tech-

Table 0.1. Techniques for imaging surface structures; TEM: transmission electron microscopy; STEM: scanning transmission electron microscopy; REM: reflection electron microscopy; SREM: scanning reflection electron microscopy; LEEM: low-energy electron microscopy; SLEEM: scanning low-energy electron microscopy; SP-LEEM: spin polarized LEEM; SEM: scanning electron microscopy; SEMP-A: SEM with polarization analysis; SAM: scanning Auger microscopy; PEEM: photoemission electron microscopy; STM: scanning tunneling microscopy; AFM: atom force microscopy; MFM: magnetic force microscopy; SNFOM: scanning near field optical microscopy; FIM: field ion microscopy; and FEM: field emission microscopy. Diffraction and analytical techniques associated with the above techniques: TED: transmission electron diffraction; EELS: electron energy-loss spectroscopy; RHEED: reflection high-energy electron diffraction; LEED: low-energy electron diffraction; TRAXS: total reflection angle X-ray spectroscopy; AES: Auger electron spectroscopy; UPS: ultraviolet photoelectron spectroscopy; XPS: soft X-ray photoemission electron spectroscopy; and EDS: energy dispersive spectroscopy.

Technique	Contrast mechanism	Resolution (nm)	Features	Chemical analysis
TEM	Diffraction and phase grating	0.2	Atomic resolution, thin film and fine particles	AES
STEM	Diffraction and phase grating	0.2	Microdiffraction, microanalysis	AES, EELS
REM	Phase and diffraction	0.5	Bulk crystals	TRAXS, EELS, AES, RHEED
SREM	Phase and diffraction	0.5	Bulk crystal, microdiffraction	TRAXS, EELS, AES, RHEED
LEEM	LEED	5	No foreshortening	
SLEEM	LEED			
SP-LEEM	Magnetic force	10	Magnetic domain	
SEM	Secondary electron	1	Topography	EDS, Auger
SEMPA	Spin scattering		Magnetic domain	
SAM	Auger electron	2	Chemical mapping	Auger
PEEM	Photoelectron	10	Work function, XPS, UPS	Energy analysis
STM	Tunneling effect	0.02 (z) 0.1 (x, y)	High resolution	
AFM	Atomic force	0.02 (z) 0.1 (x, y)	High resolution, non-conducting surface	
MFM	Magnetic force		Surface magnetic domain	
SNFOM	Photon		No surface damage	
FIM	Ionization	0.2	High resolution, depth profile	Atom probe mass spectrometer
FEM	Tunneling		Work function	



niques are LEED and AES. LEED provides a simple and convenient characterization of the surface crystallography whereas AES provides some indication of chemical composition. Table 0.2 gives a summary of the diffraction and analytical techniques that have been widely used for surface studies.

## 0.1 Historical background

The reflection electron imaging technique was first devised by Ruska (1933) shortly after the invention of TEM. This development was initiated in order to exceed the resolution limit of surface imaging by optical microscopes. Reflection electron microscopy has experienced an unsteady development (Fert and Saport, 1952; Menter, 1953; Watanabe, 1957) due to competition from other surface imaging techniques, such as scanning electron microscopy (SEM) and the replica technique for TEM. Reflection electron microscopy was advanced by Halliday and Newman (1960), who used Bragg-reflected beams in reflection high-energy electron diffraction (RHEED) patterns for REM imaging. In the 1970s, Cowley and colleagues (Cowley and Hojlund Nielsen, 1975; Hojlund Nielsen and Cowley, 1976) renewed the interest in REM with an emphasis on diffraction contrast, combining both real- and reciprocal-space analyses. A resolution of about 2 nm was achieved for directions parallel to the surface, exceeding the resolution limit of 10 nm for SEM at that time. Since then, REM has experienced rapid development due to improvement in techniques for preparing atomic flat surfaces and the introduction of ultra-high vacuum (UHV) TEMs. Applications of REM have been expanded to various fields, such as semiconductor surface reconstructions, and metal and ceramic surfaces, by many research groups (Cowley, 1986 and 1987; Bleloch *et al.*, 1987; Yagi, 1987; Hsu *et al.*, 1987; Hsu and Peng, 1987a; Yagi *et al.*, 1992; Latyshev *et al.*, 1992; Claverie *et al.*, 1992; Wang, 1993; Wang and Bentley, 1992; Uchida *et al.*, 1992a, b). In recent years, extensive theoretical calculations have been carried out to understand the basic scattering processes of high-energy (10 keV to 1 MeV) electrons from crystal surfaces in a RHEED geometry. Various other techniques, such as STM and electron holography, have been developed and used in conjunction with REM, to provide comprehensive characterization tools for surface studies. In addition, the application of REM and RHEED for *in situ* examinations of MBE growth has attracted much interest. The development of an energy-filtering system for TEM has important implications for REM and RHEED. Before the invention of this technology it was not possible to perform quantitative surface structure analysis, because only elastically scattering processes can be accurately calculated using the available theories.

Accompanying the rapid experimental progress in REM, analytical techniques, such as reflection electron energy-loss spectroscopy (REELS), have been developed.