Reflection electron microscopy and spectroscopy for surface analysis

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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.

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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
λ	The electron wavelength in free space
$\boldsymbol{p}$	The momentum of an incident electron
$\boldsymbol{K}_0$	The wavevector of an incident electron beam, $K_0=1/\lambda$
$\boldsymbol{K}$	The wavevector of a diffracted electron beam, $K=1/\lambda$
ω	Frequency
ϑ	The electron scattering semi-angle
f_α^e	The electron scattering factor of the αth atom
f_α^x	The X-ray scattering factor of the αth atom
κ	The κth atom in a crystal
$\sum_\kappa$	Sum over all atoms in crystal
$\sum_\alpha'$	Sum over atoms within the unit cell
FT	Fourier transform from real space to reciprocal space
FT^{-1}	Inverse Fourier transform
$\boldsymbol{r}$	$=(x,y,z)$. A real-space vector
$\boldsymbol{b}$	$=(x,y)$. A real-space vector
$\boldsymbol{g}$(or $\boldsymbol{h}$)	A reciprocal-lattice vector
$\boldsymbol{u}$(or $\boldsymbol{\tau}$)	A reciprocal-space vector
$V(\boldsymbol{r})$	The electrostatic potential distribution in a crystal
$V(\boldsymbol{u})$	$=\mathsf{FT}(V(\boldsymbol{r}))$. The kinematic scattering amplitude of the crystal

$V_\kappa(\boldsymbol{r})$	The electrostatic potential of the κth atom
$\rho_\kappa(\boldsymbol{r})$	The electron density distribution of the κth atom
$\boldsymbol{s}$	The scattering vector, $\boldsymbol{s}=\boldsymbol{u}/2$, $s=(\sin\vartheta)/\lambda$
Z	Atomic number
S_p	The shape function of the crystal
V_g	The Fourier coefficient of the crystal potential
$V_\alpha(\boldsymbol{g})$	The Fourier transform of the αth atom in the unit cell
$\exp(\quad W_\alpha)$	The Debye–Waller factor of the αth atom
Ω	The volume of a unit cell
$\boldsymbol{r}_\alpha$	$=\boldsymbol{r}(\alpha)$. The position of the αth atom within the unit cell
$\boldsymbol{R}_n$	The position vector of the nth unit cell
$\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$	Base vectors of the unit cell
$\boldsymbol{a}^*, \boldsymbol{b}^*, \boldsymbol{c}^*$	Base vectors of the reciprocal lattice vector
θ_g	The Bragg angle
d_g	The interplanar distance
t	Time
$\otimes$	Convolution
$T_{\mathrm{obj}}(\boldsymbol{u})$	The transfer function of the objective lens in reciprocal space
$A_{\mathrm{obj}}(\boldsymbol{u})$	The shape function of the objective aperture in reciprocal space
C_s	The spherical aberration coefficient of the objective lens
Δf	The defocus of the objective lens
Δf_c	The focus shift introduced by chromatic aberration effects
Δf_s	The Schertzer defocus
C_c	The chromatic aberration coefficient of the objective lens
ΔE	Electron energy loss
$\boldsymbol{A}$ and $\boldsymbol{B}$	Basis vectors of the crystal lattice at the surface plane
$\boldsymbol{A}_s$ and $\boldsymbol{B}_s$	Basis vectors of the surface lattice
$\boldsymbol{A}_s^*$ and $\boldsymbol{B}_s^*$	Reciprocal-lattice vectors of the surface lattice
V_s	The surface potential
N_s	The number of surface unit cells
N_1	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
θ	Surface coverage

γ	$=1[1-(v/c)^2]^{1/2}$. 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
$U(\boldsymbol{r})$	$=(2\gamma m_0 e/h^2)V(\boldsymbol{r})$, modified crystal potential
U_g	The Fourier coefficient of the modified potential U
v	The velocity of an incident electron
$\Psi(\boldsymbol{r})$	The electron wave function
$\Phi(\boldsymbol{r})$	The electron wave function excluding $\exp(2\pi i\boldsymbol{K}\cdot\boldsymbol{r})$ factor, $\Phi(\boldsymbol{r})=\Psi(\boldsymbol{r})\exp(-2\pi i\boldsymbol{K}\cdot\boldsymbol{r})$
$B_i(\boldsymbol{r})$	The ith branch Bloch wave
$\boldsymbol{k}^{(i)}$	The wavevector of the ith Bloch wave
α_i	Superposition coefficients of Bloch waves
$\boldsymbol{r}_\alpha$	The position of an atom in the unit cell
$C_g^{(i)}$	The eigenvector of the ith Bloch wave
ν_i	The eigenvalue of the ith Bloch wave
$\boldsymbol{S}_g$	Excitation error
ξ_g	Two-beam extinction distance
$\boldsymbol{R}(\boldsymbol{r})$	The static displacement vector of atoms in an imperfect crystal
$\boldsymbol{b}_B$	Burgers vectors of dislocations
σ	$=\dfrac{\pi e\gamma}{\lambda E}=\dfrac{1}{\hbar v}$
Δz	The thickness of a crystal slice
$\boldsymbol{K}_b$	The component of a wavevector in the $\boldsymbol{b}$ plane
θ	The beam's incident angle with respect to the crystal surface
φ	The beam's deviation angle parallel to the surface with respect to the zone axis
$P(\boldsymbol{b},\Delta z)$	The propagation function of a slice with thickness Δz
Q	The phase grating function of a slice with thickness Δz
d	The width of the incident beam in a perpendicular-to-surface multislice calculation
$G(\boldsymbol{r},\boldsymbol{r}')$	Green's function
$\bar{V}_0$	Average crystal inner potential
ω	Angular frequency
E_k	Electron kinetic energy
n_r	The electron refraction index at the crystal surface
$\boldsymbol{B}$	The incident beam's azimuth
ϑ_E	The characteristic angle of inelastic scattering
F	The foreshortening factor

α_{mis}	The surface mis-cut angle
$\boldsymbol{M}_{\text{t}}$	The rotation matrix
ϕ_{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
α	$= \Theta/2$, 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
$\boldsymbol{q}$ (or $\boldsymbol{Q}$)	Change in crystal wavevector
$S(\tau, \tau')$	Mixed dynamic form factor
τ	Reciprocal space vector
$\rho_{m0}(\boldsymbol{u})$	Charge density matrix
Λ	Mean-free-path length of inelastic electron scattering
$\boldsymbol{R}_n$	$= \boldsymbol{R}(n)$, the position of the nth unit cell
$\boldsymbol{u}(_{\alpha}^{n})$	The vibrational displacement of αth atom inside the nth unit cell
$\boldsymbol{r}(\alpha)$	Equilibrium position of the atom in the unit cell
$\boldsymbol{u}_{\kappa}$	The time-dependent displacement vector of the κ th atom
M_{α}	The mass of the αth atom in the unit cell
ε	The polarization vector of the phonon mode
$a^{+}(_{j}^{-\boldsymbol{q}})$	Creation operators of a phonon with wavevector $\boldsymbol{q}$ and dispersion surface ω_j
$a(_{j}^{\boldsymbol{q}})$	The annihilation operator of a phonon with wavevector $\boldsymbol{q}$ and dispersion surface ω_j
V_{α}	The time-dependent potential of the αth atom in the unit cell
$V_{0\alpha}$	The time-averaged atomic potential
ΔV	$= V - V_0$, 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
ω_{i}	The phonon frequency
$\langle n_{\text{s}} \rangle$	The average occupation number of phonon state $\lvert n_{\text{s}} \rangle$
q_{m}	The radius of the Brillouin zone
V_{BZ}	The volume of the Brillouin zone
T	Temperature
T_{D}	The Debye temperature

$\overline{a_\kappa^2}$	The mean square vibration amplitude of the κth atom
v_j	The phonon velocity
$S_{\mathrm{TDS}}(\boldsymbol{Q}, \boldsymbol{Q}')$	The scattering function in TDS
$\varepsilon(\omega, \boldsymbol{q})$	The dielectric function of a solid
$\dfrac{\mathrm{d}^2 P}{\mathrm{d}z\,\mathrm{d}\omega}$	The differential excitation probability of valence states
$\varepsilon_{\tau\tau'}(\omega)$	The generalized dielectric function
q_c	The cut-off value of a wavevector
ω_p	The resonance frequency of the volume plasmon
ω_s	The resonance frequency of the surface plasmon
$\bar{m}$	The average number of plasmons excited
$\boldsymbol{E}(\boldsymbol{r}, t)$	The electric field vector
$\boldsymbol{B}(\boldsymbol{r}, t)$	The magnetic field vector
$\boldsymbol{J}(\boldsymbol{r}, t)$	The electron current density
$\rho(\boldsymbol{r}, t)$	The electron charge density
Π	The Hertz vector
$H'(\boldsymbol{r})$	The interaction Hamiltonian
σ_{n0}	The ionization cross-section of the nth state
σ_t	The total ionization cross-section
f_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
Λ	The inelastic mean free path length
σ_I	The angular integrated ionization cross-section
Θ	Solid angle
$\mathfrak{R}$	The Rydberg energy
a_B	The Bohr radius
β	The collection semi-angle of an EELS spectrometer
Δ	The energy width of an integration window
n_A	The atom concentration
σ_{eff}	The effective angular integrated ionization cross-section
i_A	The channeling current density at atom sites
n_X	The X-ray refraction index

θ_c The critical angle for total external X-ray reflection

Sign conventions

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

Fourier transforms

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

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

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

Contents

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

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; SEMPA: 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.