Reflection Electron Microscopy and Spectroscopy for Surface Analysis

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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 1920's. 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 an TEM. In the last 60 years TEM has experienced a revolutionary development both in theory and electron optics, and has become one of the key research tools for materials characterization (Hirsch et al., 1956; Buseck et al., 1989). The point-to-point image resolution currently available in TEM is better than 0.2 nm, 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 an TEM has made it possible to form images and diffraction patterns using electrons with different energy-losses. Accurate structure analysis is possible using the purely elastically scattered electrons, the 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 devise (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 to be comparable to x-ray diffraction. A modern TEM is a versatile machine which not only can 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 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 the 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 made 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.

Surface is a special state of condensed matter, and it is the boundary of materials with 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 which 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 I compares various imaging and diffraction techniques which 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.

Table I: 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; 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; 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 forshortening	
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	Tunnelling effect	0.02 (z) 0.1 (x, y)	High resolution	
AFM	Atomic force	0.02 (z) 0.1 (x, y)	High resolution, non-conductive surface	
MFM	Magnetic force		Surface magnetic domain	
SNFOM	Photon		No surface damage	
FIM	Ionizatopm	0.2	High resolution, depth profile	Atom probe mass spectrometer
FEM	Tunneling		Work function	

For surface studies it is rarely satisfactory to use only one technique. Information regarding structure, composition and electronic structure are usually required in order to accurately determine the surface structure. Therefore, imaging techniques are usually applied in conjunction with other techniques which can provide surface sensitive chemical and electronic structures. The two most commonly used techniques are LEED and AES. LEED provides a simple and convenient characterization of the surface crystallography while AES provides some indication of chemical composition. Table II gives a summary of the diffraction and analytical techniques that have been widely used for surface studies.

Table II: Diffraction and analytical techniques for surface studies. _ indicates the most direct but not limited application of the technique.

Techniques	Atomic structure	Chemical composition	Electronic structure	Vibrational properties
Low-energy electron diffraction (LEED)	_			_
Reflection high-energy electron diffraction (RHEED)	_			_
Surface x-ray diffraction (SXRD)	_			_
X-ray photoelectron spectroscopy (XPS)	_	_	_	_
Surface extended x-ray absorption fine structure (SEXAFS)	_	_		_
Photoelectron diffraction (PhD)	_			_
Auger electron spectroscopy		_	_	
Appearance potential spectroscopy (APS)		_	_	
Ionization loss spectroscopy (ILS)		_	_	
Ultraviolet photoelectron spectroscopy (UPS)	_	_	_	
Inverse photoemission spectroscopy (IPES)			_	
Ion neutralization spectroscopy (INS)			_	
Low-energy ion scattering (LEIS)	_	_		_
High-energy ion scattering (HEIS)	_	_		_
Secondary ion mass spectroscopy (SIMS)		_		
Temperature programmed desorption (TPD)		_	_	
Electron and photon stimulated desorption (ESD and PSD)	_	_	_	
ESD ion angular distribution (ESDIAD)	_		_	_
Molecular beam scattering (MBS)	_	_		
High-resolution atom scattering (HRAS)	_	_		
Infrared reflection-absorption spectroscopy (IRAS)	_	_	_	_
High-resolution EELS (HREELS)	_	_	_	_
Reflection electron energy-loss spectroscopy (REELS)		_	_	
Transmission high-energy electron diffraction (THEED)	_			_
Total reflection angle x-ray spectroscopy (TRAXS)		_		

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 1970's, 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., 1992). 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 energy-filtering system for TEM has important implication for REM and RHEED. Before the invention of this technology it was not possible to do quantitative surface structure analysis, because only elastically scattering process 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. Both low-energy-loss and high energy-loss (Wang and Bentley, 1992) signale can be applied in determining the electronic and chemical structures of surfaces. Scanning reflection electron microscopy has been developed for imaging in-situ surface structure evolution during MBE growth. The image resolution has been improved remarkably when a field emission gun (FEG) is used.

Scope of the book

This book describes the theories, calculations, RHEED, REM, SREM and REELS experiments using reflected electrons for studying bulk crystal surfaces and surface thin films grown by MBE. The entire text was written to combine basic techniques with special applications, the theories with experiments, and the basic physics with materials science, so that a full picture about RHEED and REM is exhibited.

The book was written for graduate students and scientists who are interested in surface characterizations using reflected electron techniques. Surface scientists would find it useful for structure determinations using RHEED, REM and SREM techniques. Electron microscopist can obtain useful theories and references in applying microscopy techniques for surface studies. The book is self contained and serves as a comprehensive source of using electron microscopy and spectrometry techniques for surface studies.

Chapter 1 provides some preliminary knowledge regarding the basics of kinematical electron diffraction and imaging theory. This chapter is indispensable for understanding the basics of RHEED. The concepts introduced in this chapter will be applied in describing the scattering of crystal surfaces.

The book is composed of three parts: diffraction, imaging and spectrometry of reflected electrons. Each part is intended to give a full coverage of all the related topics. The entire text is given in a sequence so that the readers can easily follow the flow of ideas and materials.

Part A is devoted to RHEED. The basic techniques and interpretations of RHEED patterns are illustrated in chapter 2. Fundamental characteristics of RHEED and their physical basis are introduced. The two-dimensional description of surface crystallography is given, followed with surface structure determination using RHEED. The RHEED oscillation, a remarkable phenomenon for monitoring layer-by-layer crystal growth in MBE, has been described in detail. Chapter 3 addresses the main theoretical schemes for dynamical electron diffraction in RHEED geometry. Each theory is derived directly from Schrödinger equation, and its applications in RHEED calculations are illustrated. A comparison is made between the existing theories in order to illustrate their unique advantages for some particular problems. Chapter 4 concentrates on the surface resonance effect in RHEED. This effect is the most remarkable phenomenon in RHEED, which is responsible for high surface sensitivity (or monolayer resonance) of RHEED and REM. The experimental conditions under which the resonance is observed, physics of resonance, applications of the resonance effect are comprehensively described. The scattering processes of electrons from crystal surfaces under different diffracting conditions are investigated with the assistance of dynamical calculated results. The scattering picture is applied to illustrate many fundamental characteristics of REM and REELS.

Part B consists of chapters 5-8, in which the experimental techniques, contrast mechanism and applications of REM are given. Detailed experimental procedures for obtaining REM images in TEM are shown. Various effects observed in REM are described in chapter 5. Chapter 6 is designed to illustrate the imaging theory of REM, and it is the key chapter for image interpretation. The resolution of REM is discussed with consideration to electron optics and scattering geometry. Numerous examples are shown in chapters 7 and 8 illustrating the applications of REM for studying metal, semiconductor and ceramic surfaces under ultra-high-vacuum (UHV) and non-UHV conditions. The surfaces which have been studied are summarized in tables. It is demonstrated that REM is a powerful technique for in-situ imaging of surface nucleation and growth of thin films that are technologically importance.

Part C concerns the spectrometry of reflected high-energy electrons. The fundamental inelastic scattering processes in RHEED is introduced, and their applications for surface measurements are shown. The basic physics, related mathematical description, and associated applications of each process is given. Chapter 9 is about phonon scattering in RHEED, in which the kinematical and dynamical diffraction theories of thermal diffusely scattered electrons are described. Applications of valence excitations in RHEED are given in chapter 10. A complete introduction of the dielectric response theory with and without considering retardation effects is given. Examples are shown to demonstrate their applications for simulating REELS spectra. It is shown that the classical dielectric response theory gives exactly the same result as the quantum mechanical scattering theory under the first order approximation. The valence-loss spectra are applied to measure some fundamental properties associated RHEED, such as electron penetration depth into the surface and electron mean traveling distance along the surface. Chapter 11 outlines the applications of high-energy loss EELS for determining surface chemical structures. It is worth pointing out first that the EELS technique described in this book is not the high-resolution EELS, which uses an incident electron beam energy of a few eV and is sensitive to the vibration properties of surface atoms (Ibach and Mills, 1982). The EELS described here uses electrons of incident energies 30 - 400 keV. The factors which may affect the accuracy of surface chemical analysis are described in detail. Finally, chapter 12 is furnished to show the various techniques that are used in conjunction with REM, such as secondary electron imaging, surface holography and STM. Techniques which assist RHEED for solving surface structures are also demonstrated. This chapter may serve as the future developing direction of REM.

To expert in the field, the examples in this book are selected from typical studies which represent the applications of REM in a wide choice of materials. In Appendix F, a bibliography of REM, SREM and REELS is given.