HANDBOOK OF INFRARED SPECTROSCOPY OF ULTRATHIN FILMS

Valeri P. Tolstoy
Irina V. Chernyshova
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Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication Data:

Tolstoy, V. P. (Valeri P.)
Handbook of infrared spectroscopy of ultrathin films / V. P. Tolstoy, I. V. Chernyshova, V. A. Skryshevsky.
p. cm.
ISBN 0-471-35404-X (alk. paper)
1. Thin films — Optical properties. 2. Infrared spectroscopy. I. Chernyshova, I. V. (Irina V.) II. Skryshevsky, V. A. (Valeri A.) III. Title.
QC176.84.07 T65 2003
621.3815′2 — dc21

2001007192

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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PREFACE

In this book, we will designate ultrathin films, or, as they are also called in the literature, nanolayers, to mean layers ranging from submonolayers to several monolayers; these may be formed from a wide range of organic and inorganic substances or present adsorbed atoms, molecules, biological species, on a substrate or at the interface of two media. These films play an important role in many current areas of research in science and technology, such as submicroelectronics, optoelectronics, optics, bioscience, flotation, materials science of catalysts, sorbents, pigments, protective and passivating coatings, and sensors. It could even be argued that the rapid advances in thin-film technology has necessitated the development of special approaches in the synthesis and investigation of nanolayers and superlattices. Nowadays, these approaches are generally applicable in so-called nanotechnology, which includes the synthesis–deposition and characterization of ultrathin films with a prescribed composition, morphology–architecture and thicknesses on the order of 1 nm.

Common features in all studies in the field of nanotechnology arise from problems connected with the physicochemical investigation of ultrathin films, which originate in general from their extremely small thickness. To solve these problems, a number of technically complicated physical methods that operate under UHV conditions, such as AES, XPS, LEED, HREELS are used. Infrared (IR) spectroscopy and in particular Fourier transform IR (FTIR) spectroscopy — a method that enables the determination of molecular composition and structure — offers important advantages in that the measurements can be carried out for nanolayers located not only on a solid substrate but also at solid–gaseous, solid–liquid, liquid–gaseous, and solid–solid interfaces, including semiconductor–semiconductor, semiconductor–dielectric, or semiconductor–metal, with no destruction of either medium. Thus IR spectroscopy is one of a few physical methods that can be used for both in situ studies of various processes on surface and at interfaces and technological monitoring of thin-film structures in fields such as microelectronics or optoelectronics under serial production conditions. The versatility of modern FTIR spectroscopy provides means to characterize ultrathin coatings on both oversized objects (e.g., works of art) and small (10–20-μm) single particles, substrates with unusual shapes (e.g., electronic boards), and recessed areas (e.g., internal surfaces of tubes). It should be emphasized that IR spectroscopy can be highly sensitive to ultrathin films: Depending on the system, the sensitivity is 10^{-5}–10% monolayer.

However, the various IR spectroscopy techniques must be adapted to measure spectra of very small amounts of substance in the form of ultrathin films. While for analyses of bulk materials it is possible to select the optimum mass of substance to record its spectrum, in the case of ultrathin films it is only possible to vary the conditions under which the spectra are recorded (measurement technique, polarization, angle of incidence, immersion media, number of radiation passages through the sample). For this purpose, it is necessary first to theoretically assess the effect of the recording conditions on the intensity of the absorption bands.

By understanding optical theory for stratified media, it is also possible to distinguish optical effects (artifacts), which present in each IR spectrum of an ultrathin film, and, hence, to avoid misinterpretation of the experimental data.

Although the optimum conditions for a number of simple systems are known (e.g., for ultrathin films on metals reflection–absorption (IRRAS) at grazing angles of incidence is commonly used, and for ultrathin films on transparent substrates, multiple internal reflection (MIR) is most suitable in many cases), the spectral contrast can be further enhanced by employing additional special technical approaches.

The material in this handbook is presented in such a way as to address these issues. Thus, the theoretical concepts associated with the interaction of IR radiation with matter and with thin films are considered and, to evaluate the optimum conditions routinely, simple algorithms for programming are given in Chapter 1. In Chapter 2, a theoretical evaluation of the optimum conditions for measuring nanolayer spectra is presented. In Chapter 3, a more detailed interpretation of the IR spectra of ultrathin films on flat and powdered substrates is discussed from the viewpoint of optical theory, including the authors' methods of determination of the optical constants of ultrathin films [1, 2] and molecular orientation [3]. In Chapter 4, technical approaches to measure good-quality IR spectra of ultrathin films are considered. Along with the techniques considered routine for studies of ultrathin films in many laboratories and original techniques described in the literature, techniques developed by the authors are included here, namely IR spectroscopy of single and multiple transmission in *p*-polarized radiation [4, 5]; IRRAS of the surface of semiconductors and dielectrics [6]; IRRAS of metals, semiconductors, and dielectrics in immersion media [7, 8]; diffuse transmission of disperse materials [9, 10]; and the special attenuated total reflection (ATR) technique for studying the semiconductor–solution interface [11]. An important feature of the optical accessories described is that they are placed in the sample compartment of a conventional continuous-scan or step-scan FTIR spectrometer, without any change in the spectrometer optical scheme. In addition, different attachments for specialized measurements are considered, including IR microscope objectives, in situ chambers, and spectroelectrochemical cells. Time-resolved spectroscopy and enhanced surface and structure sensitivity in IR spectroscopic techniques such as modulation spectroscopy and two-dimensional correlation analysis are described. Subsequent chapters illustrate some applications of these techniques in the study of thin-layer structures and semiconductor–electrolyte interfaces, which are currently of great practical significance in electronics, solar energy storage, sensors, catalysis, bioscience, flotation, and corrosion inhibition. Recommendations are given regarding application of these techniques for automated and on-line analysis of thin-film structures. PAS [12, 13] are not included here, because its sensitivity is insufficient for the measurements in question. Infrared emission studies of ultrathin films have recently been reviewed [14, 15]. Since this method, although rather surface sensitive under specific conditions, has not yet experienced extensive application, it is not considered here as well. Instead, fundamentals and techniques of transmission, diffuse transmission, IRRAS, ATR, and DRIFTS methods will be presented, with emphasis on their application to ultrathin films. Complementary information on how to use these methods and their history may be found in other monographs [16–21].

It should be noted that because the material is presented in such a manner, this monograph may serve as a handbook. It includes the theoretical foundations for the interaction of IR radiation with thin films, as well as the optimum conditions of measuring spectra of various systems, which are analyzed by computer experiments and illustrated by specific examples. Complementary to this, the basic literature devoted to the application of IR spectroscopy in the investigation of nanolayers of solids and interfaces is presented, and the necessary reference material for the interpretation of spectra is tabulated. Thus this book will be extremely useful for any laboratory employing IR spectroscopy, and for each industrial firm involved in the production of thin-film structures, as well as by final-year and postgraduate students specializing in the fields of optics, spectroscopy, or semiconductor technology.

Dr. Valeri Tolstoy (St. Petersburg State University, Russia) authored Chapter 2 and Sections 3.5, 3.10, 4.1.1, 4.1.2, 4.2.1, 4.2.2, 4.4, 4.5, 7.1–7.3. Dr. Irina Chernyshova (St. Petersburg State Polytechnical University, Russia) wrote Chapters 1, 3, 4, and 7 (except for the sections mentioned above) and coauthored Sections 2.3, 2.5, and 2.7. Prof. Valeri Skryshevsky (Kyiv National Taras Shevchenko University, Ukraine) presents Chapters 5 and 6. Tables in the Appendix were collected by Valeri Tolstoy and Irina Chernyshova. The language and style were edited by Dr. Roberta Silerova (University of Saskatchewan, Canada). Dr. Nadezhda Reutova (St. Petersburg State University, Russia) translated into English Chapters 2, 5, and 6 and Sections 3.3–3.5, 3.10, 4.1, and 4.2, and helped with translation of Chapter 1 and Sections 3.1 and 3.2.

Acknowledgements

We thank Dr. Silerova for editing the English language, improving the handbook style, and her great patience during the joint work several years long; Dr. Reutova

for translating part of the text into English; and all the authors who have permitted citation of their results. VPT acknowledges a partial financial support granted by Interfanional Scientific Foundation (USA), Russian Foundation for Basic Research (RFBR), and Civilian Research and Development Foundation (CRDF) (USA). IVC thanks RFBR, the Swedish Institute, and Elena Chernetskaya. VAS thanks Ministry of Ukraine for Education and Science. We all thank friends and relatives who helped us with this work.

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VALERI TOLSTOY
IRINA CHERNYSHOVA
VALERI SKRYSHEVSKY

ACRONYMS AND SYMBOLS

A/D	analog–digital (convertor)
AES	Auger electron spectroscopy
AFM	atomic force microscopy
ARUPS	angle-resolved UV photoelectron spectroscopy
ATR	attenuated total reflection
AU	arbitrary units
AW	air–water (interface)
BF	Bruggeman formula
bi CMOS	bipolar and complementary MOS
BLB	Bouguer–Lambert–Beer (law)
BM	Bruggeman model
BML	buried metal layer
BP	bandpass
CMC	critical micelle concentration
CMLL	Clausius–Mossotti/Lorentz–Lorenz (model)
CMP	chemomechanical polishing
CS	compressed solid (L monolayer phase)
CVD	chemical vapor deposition
DA	Drude absorption, dispersion analysis
DAC	diamond anvil cell
DCT	dielectric continuum theory
DF	distribution function
DL	double layer
DMA	dynamic mechanical analysis
DR	diffuse reflection
DR	dichroic ratio
DRIFTS	diffuse reflectance infrared Fourier transform spectroscopy
DT	diffuse transmission
DTA	differential thermal analysis
DTGS	deuterated triglicine sulfate (detector)
DTIFTS	diffuse transmittance infrared Fourier transform spectroscopy

EDS	energy dispersive X-ray spectroscopy
EELS	electron energy loss spectroscopy
EFA	electric field analysis
EIRE	extended internal reflection element
EMIRS	electrochemically modulated infrared spectroscopy
EMT	effective medium theory
ERS	external reflection spectroscopy
EWAS	evanescent wave absorption spectroscopy
EXAFS	extended X-ray absorption fine-structure
FET	field-effect transistor
FPA	focal plane array
FTEMIRS	Fourier transform EMIRS
μ-FTIR	Fourier transform infrared microscopy
FTIR	Fourier transform infrared spectroscopy
FWHM	full width at half maximum
GIR	grazing internal reflection
GIXD	grazing-incidence X-ray diffraction
H/D	hydrogen/deuterium (exchange)
HATR	horizontal ATR
HL	Helmholtz layer
HM	hemimicelle model
HP	highpass
HPLC	high performance liquid chromatography
HREELS	high resolution electron energy loss spectroscopy
IC	integrated circuit
ILD	infrared linear dichroism
IOW	integrated optical waveguide
IP	in-phase
IR	infrared
IRE	internal reflection element
IRRAS	infrared reflection absorption spectroscopy
ITO	indium tin oxide
KK	Kramers–Krönig
KM	Kubelka–Munk
L monolayer	Langmuir monolayer
LB film	Langmuir–Blodgett film
LC	liquid condensed (L monolayer phase)
LE	liquid expanded (L monolayer phase)
LED	light-emitting data
LEED	low-energy electron diffraction
LIA	lock-in-amplifier
LO	longitudinal optical
LP	lowpass
LPD	liquid-phase deposition
LST	Lyddane–Sachs–Teller (law)

LT-OTTE	low-temperature OTTE
LUMO	lowest unoccupied molecular orbital
MAS NMR	magic angle spinning NMR
MBE	molecular beam epitaxy
MCT	mercury-cadmium-tellurium
MG	Maxwell–Garnett (dielectric function)
MGEMT	Maxwell–Garnett effective medium theory
MIR	multiple internal reflection
MIRE	multireflection internal reflection element
MIS	metal insulator semiconductor
MIT	multiple internal transition
ML	monolayer
MO	molecular orientation
MOATR	metal-overlayer ATR
MOS	metal–oxide–semiconductor
MOSFET	metal–oxide–semiconductor FET
MP	monolayer packing
MSEF	mean-square electric field
MTC	monothiocarbonate
NEXAFS	near-edge X-ray absorption fine structure
NIR	near IR
NMR	nuclear magnetic resonance
NMSEF	normalized mean-square electric field
OCP	open-circuit potential
ODT	order–disorder transition
OTE	optically transparent electrode
OTTLE	optically transparent thin-layer electrochemical (cell)
PAS	photoacoustic spectroscopy
PCA	principal component analysis
PDIR	potential-difference infrared (spectroscopy)
PECVD	plasma enhanced vapor deposition
PEDR	Perkin–Elmer diffuse reflectance
PEM	photoelestic modulator
PET	poly(ethylene teriphtalate)
PFPE	perfluoropolyesther
PM	polarization modulation
PMMA	poly(methyl methacrylate)
PSTM	photon STM
PTFE	poly(tetrafluoroethylene)
PVA	poly(vinyl acetate)
PVC	poly(vinyl chloride)
PVD	physical vapor deposition
Q	quadrature
QCM	quartz crystal microbalance
RA	reflectance-absorbance

RBS	Rutherford backscattering
RH	relative humidity
RTPM	real-time PM
S^2	step-scan
SAM	self-assembled monolayer
SAW	surface acoustic wave
SCE	saturated calomel electrode
SCR	space charge region
SE	semiconductor electrode
SEC	spectroelectrochemical
SEIRA	surface enhanced infrared absorption
SEM	scanning electron microscopy
SERS	surface enhanced Raman spectroscopy
SEW	surface electromagnetic waves
SFG	sum frequency generation
SHE	standard hydrogen electrode
SHG	second harmonic generation
SI	international system of units
SIA	sequential implantation and annealing
SIMOX	separation by implanted oxygen
SIMS	secondary ion mass spectrometry
SIPOS	semi-insulating polycrystalline silicon
SNIFTIRS	subtractively normalized interfacial FTIR spectroscopy
SNOM	scanning near field optical microscopy
SNR	signal-to-noise ratio
SOI	silicon-on-insulator
SPAIRS	single potential alternation IR spectroscopy
SPR	surface plasmon resonance
SSR	surface selection rule
STIRS	surface titration by internal reflectance spectroscopy
STM	scanning tunneling microscopy
STPD	stepwise thermo-programmed desorption
TDM	transitional dipole moment
TEM	transmission electron spectroscopy
TG	thermogravimetry
TIRF	total internal reflection fluorescence
TLC	thin layer chromatography
TMOS	tetraethylorthosilicate
TO	transverse optical
TPD	temperature programmed desorption
TR	time resolution
UHV	ultra high vacuum
ULSC	ultra large scale circuit
ULSI	ultra large scale integrated
UV	ultraviolet (radiation)

VLSI	very large scale integrated
VPE	vapor phase epitaxy
WAXS	wide-angle X-ray scattering
X, EX, BX, AX	xanthate (ethyl-, *n*-butyl-, amyl-)
XANES	X-ray absorption near-edge structure
XPS	X-ray photoelectron spectroscopy
2D IR	two dimensional correlation analysis of IR dynamic spectra

Symbols

$\hat{\alpha}$	Electric polarizability
α	Decay constant≡absorption coefficient
β	Restoring force
γ	Tilt angle, damping constant
δ	Bending mode
ε	Permittivity≡dielectric constant≡dielectric function
ε_{∞}	High-frequency dielectric constant≡screening factor
ε_m	Permittivity of metal
$\varepsilon_{\mathrm{sm}}$	Permittivity of surrounding medium
$\varepsilon_{\mathrm{st}}$	Static (low-frequency) dielectric constant
θ	Angle of bond
λ	Wavelength
μ	Permeability
ν	Wavenumber, Stretching mode
ρ	Mass volume density, resistivity, rocking mode
$\boldsymbol{\rho}$	Dynamic dipole moment
σ	Electrical conductivity
τ	Time
φ_1 or φ	Angle of incidence
ω	Wagging mode, angular velocity
ω_p	Plasma frequency
A	Absorbance
$\mathbf{B}$	Magnetic induction
c	Velocity of light
C	Volume/mass concentration
d	Thickness
$\mathbf{D}$	Electric displacement
d_p	Penetration depth
$\mathbf{E}$	Electric field
E	Electrode potential, electric field
E_g	Energy gap
E	Integrated molar absorption coefficient
f	Filling fraction
g_k	Geometric factor

h	Plank constant
$\mathbf{H}$	Magnetic field
I	Intensity of radiation
$\mathbf{j}$	Current density
k	Extinction coefficient≡absorption index
$\mathbf{k}$	Wave vector
m	Mass
$\mathbf{M}$	Magnetic polarization
N	Surface or volume density of molecules (atoms), number of reflections
n	Refractive index
$\mathbf{p}$	Dipole moment
$\mathbf{P}$	Electric polarization
r	Reflection coefficient
R	Reflectance
S	Oscillator strength
t	Time/transmission coefficient
T	Temperature/transmittance
$\mathbf{v}$	Velocity

INTRODUCTION

In the infrared (IR) spectroscopic range (200–4000 cm^{-1}), radiation is generally characterized by its wavenumber ν (cm^{-1}), related to the wavelength λ (μm), frequency $\tilde{\nu}$ (s^{-1}), and angular frequency ω (s^{-1}) as

$$\nu = \frac{1}{\lambda} = \frac{\tilde{\nu}}{c} = \frac{\omega}{2\pi c}, \tag{1}$$

where $c = 2.99793 \times 10^8$ m·s^{-1} is the velocity of electromagnetic radiation in a vacuum.

When IR radiation containing a broad range of frequencies passes through a sample, which can be represented as a system of oscillators with resonance frequencies $\nu_{0,i}$, then according to the Bohr rule,

$$\Delta E = h\nu \tag{2}$$

(where ΔE is the difference between the energy of the oscillator in the excited and ground states, ν is the frequency of photons, and $h = 6.626069 \times 10^{-34}$ J·s is Planck's constant), photons with frequencies $\nu = \nu_{0,i}$ will be absorbed. These photons will be eliminated from the initial composition of the radiation. Since all the elementary excitations have unique energy levels (*fingerprints*), measurements of the disappearing energy as a function of ν (*absorption spectrum* of the sample) enable these excitations to be identified, and microscopic information about the sample (e.g., molecular identity and conformation, intra- and intermolecular interactions, or crystal-field effects, etc.) may be obtained.[†]

[†] See M. Hollas, *Fundamental Aspects of Vibrational Spectroscopy. Modern Spectroscopy*, 3rd ed., Wiley, Chichester, 1996.

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ABSORPTION AND REFLECTION OF INFRARED RADIATION BY ULTRATHIN FILMS

The primary characteristics that one identifies from infrared (IR) spectra of ultrathin films for further analysis are the resonance frequencies, oscillator strengths (extinction coefficients), and damping (bandwidths), related to different kinds of vibrational, translational, and frustrated rotational motion inside the thin-film material [1–7]. However, the microscopic processes inside or at the surface of a film (motion of atoms and electrons) give rise to the frequency dependence (the *dispersion*) not only of the extinction coefficient but also of the refractive index of the film. As a result, a real IR spectrum of an ultrathin film is, as a rule, distorted by so-called *optical effects*. Specifically, the spectrum strongly depends upon the conditions of the measurement, the film thickness, and the optical parameters of the surroundings and substrate impeding extraction of physically meaningful information from the spectrum. Thus after introduction of the nomenclature accepted in optical spectroscopy and a brief discussion of the physical mechanisms responsible for absorption by solids on a qualitative level, this introductory chapter will concentrate on the basic *macroscopic* or *phenomenological* theory of the optical response of an ultrathin film immobilized on a surface or at an interface.

The theoretical analysis of the IR spectra of ultrathin films on various substrates and at interfaces will involve two assumptions: (1) the problem is linear and (2) the system under investigation is macroscopic; that is, one can use the macroscopic Maxwell formulas containing the local permittivity. The first assumption is valid only for weak fields. The second assumption means that the volume considered for averaging, a (the volume in which the local permittivity is formed), is lower than the parameter of inhomogeneity of the medium, d (e.g., the effective thickness of the film, the size of islands, or an effective dimension of polariton), $a < d$. In this case, the response of the medium to the external electromagnetic field is essentially the response of a continuum. The description of the medium properties using the macroscopic permittivity is called the dielectric continuum theory (DCT). One issue discussed repeatedly in the literature is the correctness of the DCT approximation for spectra of ultrathin films. In this context, semiphenomenological and microscopic models establishing the correlation between local field effects, molecular and atomic dynamics, and the IR spectrum of the film on the surface were proposed (for reviews, see Refs. [1, 6, 7]). These models greatly enhance the understanding of ultrathin films of submonolayer coverage. However, the corresponding relationships are cumbersome, deal with specific (as a rule, vacuum–metal) interfaces, require further refinements for most of the systems studied, and, hence, are unfeasible for routine analysis of the spectra. On the other hand, the macroscopic relationships can be used without substantial difficulties to solve many problems arising in the spectroscopy of ultrathin films. First, they allow one to choose the optimum conditions for recording IR spectra by comparing band intensities (Chapter 2), which is of prime technical importance. Second, by using spectral simulations based on the macroscopic formulas, it is possible to distinguish optical effects from physicochemical effects in the film, such as film inhomogeneity (porosity) and changes in the orientation of the film species (Chapter 3).

1.1. MACROSCOPIC THEORY OF PROPAGATION OF ELECTROMAGNETIC WAVES IN INFINITE MEDIUM

Optical thin-film theory is essentially based on the *Maxwell theory* (1864) [8], which summarizes all the empirical knowledge on electromagnetic phenomena. Light propagation, absorption, reflection, and emission by a film can be explained based on the concept of the *macroscopic* dielectric function of the film material. In this section, we will present the results of the Maxwell theory relating to an infinite medium and introduce the nomenclature used in the following sections dealing with absorption and reflection phenomena in layered media. The basic assertions of macroscopic electrodynamic theory can be found in numerous textbooks (see, e.g., Refs. [9–16]).

1.1.1°. The optical properties of an infinite medium without any electric charge other than that due to polarization are described by Maxwell's equations [in International System (SI) of units]:

$$\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{1.1a}$$

$$\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \hat{\sigma}\mathbf{E}, \tag{1.1b}$$

$$\nabla \cdot \mathbf{D} = 0, \tag{1.1c}$$

$$\nabla \cdot \mathbf{B} = 0. \tag{1.1d}$$

Here, **E** and **H** are, respectively, the vectors of the macroscopic electric and the magnetic field; $\varepsilon_0 = 8.854 \times 10^{-12}\mathrm{C{\cdot}N^{-1}{\cdot}m^{-2}}$ and $\mu_0 = 4\pi \times 10^{-7}\mathrm{N{\cdot}A^{-2}}$ are