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Olaf Stenzel

The Physics of Thin Film Optical Spectra

An Introduction

Second Edition

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The Physics of Thin Film Optical Spectra

An Introduction

Second Edition

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To Gabi

Brookite Crystal

Detail of a painting by Brenda Mary Doherty, an Irish master student of photonics at Abbe School of Photonics, Friedrich Schiller University Jena, Germany. Printed with permission.

Brookite is one of the naturally occurring polymorphs of titanium dioxide, a widely used high index coating material.

Foreword

When we open a new textbook, it is very helpful for us to learn from the very beginning answers to the following two major questions: First, what area is covered by this book, and how it relates to a reader's personal area of expertise or his/her planned research area, if the reader is still a university student. Second, how well the content of the book is presented, and how much effort will be required to extract required knowledge from the book. Below, I will try to answer both of these questions.

Never before had modern science and technology been as interdisciplinary as they are now, and this is fueling a high demand for textbooks that address topics of common interest for wide groups of students who later in their lives will work in quite differing research and applications areas. In particular, thin-film optics is one topic that is of great importance for physical chemistry, material science, optoelectronics, photonics, solar energy conversion, physical optics, semiconductor physics and lasers. This book will be useful not only for master and postgraduate students preparing themselves for work in those areas, but also for scientists and engineers who already possess considerable knowledge of thin-film optics. The content of the book is connected with material and geometrical aspects of thin-film optical spectra, and these aspects are covered with unprecedented width and depth. Under one cover, the textbook summarizes a lot of facts and results that are scattered over a great number of manuscripts and textbooks on spectroscopy, optics, nonlinear optics, electrodynamics, solid-state physics, theoretical physics, etc. It presents a fundamental description of thin-film optical spectra and main mechanisms responsible for the optical properties of thin solid films. Along with isotropic thin films, the textbook also discusses optical properties of more complicated structures such as thin films with diffraction gratings, metal-island films, gradient-index films, anisotropic films and birefringent optics, multilayer systems and dispersive mirrors. This implies its special relevance to various practical aspects of thin-film optics and spectroscopy.

The textbook is written in a style that I personally consider to be the best and the most appropriate one for successful learning of modern interdisciplinary subjects.

This style combines an appeal to a physicist's intuition and understanding with a high-level mathematical treatment. All new topics begin with detailed explanations of respective basic ideas in physics. These explanations are oriented toward understanding of physical phenomena, while mathematical derivations follow later. In fact, many of these derivations may be skipped at the first reading, and the reader can go back to them after acquainting with the main results of the studied topic. Everywhere throughout the text, there are carefully selected excellent examples of experiments that illustrate main results and their applications. On the whole, the text is easy to read, especially for a reader with basic knowledge at the level of bachelor's physics degree.

Everybody, who has ever given lectures to students, knows how a lecture course gets modified and polished year by year, not only because of the direct feedback from students, but also due to the lecturer's personal intuitive feeling of listeners' reaction to the lectures. The main content of the textbook has been presented to university students for many years, and this has obviously had a very positive effect on the style of the text and its organization. I really enjoyed reading this textbook, and I hope that many readers will share this feeling with me.

Moscow Alexander Tikhonravov

Preface to the Second Edition

In fall 2014, Claus Ascheron (Springer-Verlag) asked me to consider a second extended and updated edition of the present textbook. I was very grateful for this possibility, and therefore I quickly agreed to that proposal because of several reasons:

- From the appearance of the first edition in 2005, I have got positive and stimulating feedback from readers including students, scientists, and even lecturers. This feedback was very important for me, because it convinced me that my original idea of writing a pure textbook about the basics of thin-film optics and spectroscopy, including the mathematical derivations of all formulas and combining them with the illustration of the underlying physical concepts, was correct and useful. It is therefore my pleasure to improve, update, and correct parts of this textbook, while preserving the original didactic concept and logical detail of the text.
- I am very grateful to Prof. Andreas Tünnermann, Fraunhofer IOF Jena and Friedrich Schiller University (FSU) Jena, for giving me the regular possibility for composing and reading a lecture course on Thin Film Optics at Abbe School of Photonics, FSU Jena. I have been giving these lectures every year for master students of physics or photonics, starting from 2009. These students (who practically come from all over the world) provide a further vital source of critical feedback to my Thin Film Optics course. It was my pleasure to modify or change certain illustrations or derivations in this textbook as a result of this fruitful cooperation with my students.
- Over the years of teaching, I was able to detect several errors of small or medium significance, as well as some insufficient, inappropriate, or sometimes misleading explanations in the original (first) edition. The second edition supplies a highly welcome and suitable frame for improving the text and figures where possible.
- At the time when the first edition of this book appeared, a german student of physics usually finished his study obtaining the degree of a diploma physicist (Diplomphysiker). Today, the study is subdivided into two sections: a first one

which is finished by obtaining the Bachelor degree, and a second one for obtaining the master degree. It is not my duty to judge the sense or non-sense of this change, anyway a textbook written for use in a university course must consider this development at least when defining the pursued audience. Therefore I spent some time on the study of modern textbooks on physics written for use in the Bachelor period. I have come to the conclusion that the present textbook should be useful for anyone who has already obtained the Bachelor degree in physics, i.e., Bachelor knowledge should be sufficient to benefit from reading this book. I am grateful to Springer-Verlag and Walter de Gruyter GmbH for the generous supply of complimentary lecturer copies of several relevant modern textbooks.

- It is one thing to supply the reader with derivations of all the equations which are so useful in thin-film optics practice. The other thing is to provide suitable practical examples which verify the relevance of the theoretical approaches in practice. When having flipped through the book you may have obtained the feeling that my primary strength is not of experimental nature—I may convince you that you are absolutely right with that. It is more important for me to cooperate with highly skilled experimentators, who have at the same time strongest theoretical background, and are ready to get the most out of their experimental setups to demonstrate the superior use of a coherent interaction of experimental and theoretical efforts. It was one of the basic shortcomings of the first edition that I had not yet established such cooperations so that the practical examples might have been not so convincing. When preparing the second edition, I had the privilege to benefit from an extremely fruitful cooperation with Steffen Wilbrandt (IOF), who supplied me with high quality experimental samples prepared by electron beam evaporation without or with plasma assistance. I am also grateful to Hanno Heiße, Heidi Haase, and Josephine Wolf for corresponding technical assistance. Mikhael Trubetskov, OptiLayer GmbH, was kind enough to provide me with selected design calculations for dispersive mirrors. Experimental material concerning sputtered double band rugate filters has been contributed by Peter Frach and co-workers, Fraunhofer FEP.

My thanks are due to all of the mentioned persons, without their effort I would not have been able to provide these practical examples.

I would like to emphasize it once more in this context, that the present book is intended to serve as a textbook for introducing the reader into the fundamentals of thin film optics. From the first edition of this book, to my knowledge, these fundamentals have not changed. Therefore, the reference list at the end of this second edition is practically the same as in the first edition. Any updates rather concern the practical examples, and for convenience, in these cases the corresponding references have directly been included into the main text. So that the references scattered through the text refer to the sources of concrete (experimental) examples, while the reference chapter at the end of this book summarizes primary literature relevant for understanding the fundamentals.

In 2014, I authored another monograph entitled “Optical Coatings: Material Aspects in Theory and Practice”, Springer 2014. That monograph stresses a more phenomenological and illustrative approach to the material side of thin-film optics; it is not a textbook, instead it is rather complimentary to the present book by both content and logical approach, except of course some necessary overlap when reviewing the basics. None of these two books shall and can replace the other one: If you are seeking for a quantitative approach and its derivation, read the present book, if you are seeking for a coherent illustration on how this quantitative approach appears to be reflected in practice, read the other. Or even better, read both of them.

But I would like to turn your attention to a last aspect: Surface optics and thin-film optics are interdisciplinary and of highest practical relevance. They have strongest impact on our daily life and benefit from the sometimes challenging feedback they have generated. It is one of my passions therefore to look on artwork, literature and even landscapes through the eyes of a thin film physicist: Seeking and finding stimulating allusions and analogies between art and sciences. Therefore, I had pleasure including plenty of relevant classical literature citations into the “material aspects” book. In the present book, instead, artwork created by local Jena artists is used to provide an atmospherical background to the corresponding book chapters. I am so grateful to Brenda Mary Doherty and Astrid Leiterer for permission to present their beautiful pictures or sculptures here in a scientific context. Alexander Stendal provided me with several drawings highlighting the essence of wave propagation in inhomogeneous or dispersive media from daily experience.

Finally, I would like to express my deepest thanks to Prof. Alexander Tikhonravov, the head of the Research Computing Center of M.V. Lomonosov Moscow State University (MSU) and one of my teachers from my studying times, for supplying a concise and elaborate foreword to the present edition of this book. In addition to his scientific reputation, I highly appreciate Alexander as a university teacher, so that this foreword does not only provide valuable information to the potential reader of this book, but is also a very encouraging and stimulating feedback to me.

Jena Olaf Stenzel

Preface to the First Edition

The present monograph represents itself a tutorial to the field of optical properties of thin solid films. It is neither a handbook for the thin-film practitioner, nor an introduction to interference coatings design, nor a review on the latest developments in the field. Instead, it is a textbook which shall bridge the gap between ground level knowledge on optics, electrodynamics, quantum mechanics, and solid state physics on one hand, and the more specialized level of knowledge presumed in typical thin-film optical research papers on the other hand.

In writing this preface, I feel it makes sense to comment on three points, which seem to me equally important. They arise from the following (mutually interconnected) three questions:

1. Who can benefit from reading this book?
2. What is the origin of the particular material selection in this book?
3. Who encouraged and supported me in writing this book?

Let me start with the first question, the intended readership of this book. It should be of use for anybody, who is involved into the analysis of optical spectra of a thin-film sample, no matter whether the sample has been prepared for optical or other applications. Thin-film spectroscopy may be relevant in semiconductor physics, solar cell development, physical chemistry, optoelectronics, and optical coatings development, to give just a few examples. The book supplies the reader with the necessary theoretical apparatus for understanding and modeling the features of the recorded transmission and reflection spectra.

Concerning the presumed level of knowledge one should have before reading this book, the reader should have some idea on Maxwell's equations and boundary conditions, should know what a Hamiltonian is and for what it is good to solve Schrödinger's equation. Finally, basic knowledge on the band structure of crystalline solids is presumed. The book should thus be understandable to anybody who listened the ground courses in physics at any university.

The material selection was strongly influenced always by the individual experience on working with and supervising physics students as well as Ph.D. students.

To a large extent, it stems from teaching activities at Chemnitz University of Technology, Institute of Physics, where I was involved into university research on thin-film properties, and read several courses on applied spectroscopy topics as a lecturer. This university time stands for the more “academic” features of the book. It must be mentioned, that in that time I authored a textbook on thin-film optics in German “Das Dünnschichtspektrum” with emphasis on the formal treatment of the optical response of thin solid films. But the present monograph is by no means a translation of that German book. The reason is, that in fall 2001, I changed to the Optical Coating Department at the Fraunhofer Institute of Applied Optics and Precision Engineering (IOF) in Jena, Germany. From that time, my working field shifted to more applied research projects on the development of optical coatings, primarily for the visible or near infrared spectral regions. It is the *combination* of university teaching until 2001 with more applied research work at the Fraunhofer Institute, which defines the individual content and style of the present monograph.

Finally, let me acknowledge the support of colleagues, co-workers, and friends in writing this book. First of all, I acknowledge Dr. Claus Ascheron and Dr. Norbert Kaiser for encouraging me to write it. Thanks are due to Dr. Norbert Kaiser for critical reading of several parts of the manuscript. The book could never have been written without the technical assistance by Ellen Kämpfer, who took the part of writing plenty of equations, formatting graphics and finally the whole text to make the manuscript publishable. Further technical support was supplied by Martin Bischoff.

Concerning the practical examples integrated into this book, e.g., the measured optical spectra of organic and inorganic thin-solid films, so it should be emphasized that all of them have been obtained in the course of research work at Chemnitz University (until summer 2001) and the Fraunhofer IOF (from fall 2001). Therefore, thanks are due to the former members of the (unfortunately no more existing) research group on thin-film spectroscopy (at Chemnitz University of Technology, Institute of Physics, Department of Optical Spectroscopy and Molecular Physics), and to the researchers in the Optical Coatings Department of the Fraunhofer IOF in Jena. The book benefited from the stimulating research atmosphere in these facilities.

Jena Olaf Stenzel

Contents

1 Introduction . . . 1
- 1.1 General Remarks . . . 1
- 1.2 To the Content of the Book . . . 2
- 1.3 The General Problem . . . 4
- 1.4 One Remark Concerning Conventions . . . 6

Part I Classical Description of the Interaction of Light with Matter

2 The Linear Dielectric Susceptibility . . . 11
- 2.1 Maxwell's Equations . . . 11
- 2.2 The Linear Dielectric Susceptibility . . . 13
- 2.3 Linear Optical Constants . . . 15
- 2.4 Some General Remarks . . . 18
- 2.5 Example: Orientation Polarization and Debye's Equations . . . 19
- 2.6 Energy Dissipation . . . 23

3 The Classical Treatment of Free and Bound Charge Carriers . . . 25
- 3.1 Free Charge Carriers . . . 25
  - 3.1.1 Derivation of Drude's Formula I . . . 25
  - 3.1.2 Derivation of Drude's Formula II . . . 28
- 3.2 The Oscillator Model for Bound Charge Carriers . . . 31
  - 3.2.1 General Idea . . . 31
  - 3.2.2 Microscopic Fields . . . 33
  - 3.2.3 The Clausius-Mossotti and Lorentz-Lorenz-Equations . . . 35
- 3.3 Probing Matter in Different Spectral Regions . . . 39
- 3.4 Spatial Dispersion . . . 39
- 3.5 Attempt of an Illustrative Approach . . . 42

4 Derivations from the Oscillator Model 47
4.1 Natural Linewidth 47
4.2 Homogeneous and Inhomogeneous Line Broadening Mechanisms 49
4.2.1 General 49
4.2.2 Collision Broadening 50
4.2.3 Doppler Broadening 50
4.2.4 Brendel Model 51
4.3 Oscillators with More Than One Degree of Freedom 52
4.4 Sellmeier's and Cauchy's Formulae 54
4.5 Optical Properties of Mixtures 57
4.5.1 Motivation and Example 57
4.5.2 The Maxwell Garnett, Bruggeman and Lorentz-Lorenz Mixing Models 61
4.5.3 Metal-Dielectric Mixtures and Remarks on Surface Plasmons 64
4.5.4 Dielectric Mixtures and Wiener Bounds 67
4.5.5 The Effect of Pores 72
4.5.6 The Refractive Index of Amorphous Silicon in Terms of the Lorentz-Lorenz Approach: A Model Calculation 78

5 The Kramers-Kronig Relations 85
5.1 Derivation of the Kramers-Kronig Relations 85
5.2 Some Conclusions 89
5.3 Resume from Chaps. 2–4 and this Chapter 91
5.3.1 Overview on Main Results 91
5.3.2 Problems 92

Part II Interface Reflection and Interference Phenomena in Thin Film Systems

6 Planar Interfaces 97
6.1 Transmission, Reflection, Absorption and Scattering 97
6.1.1 Definitions 97
6.1.2 Experimental Aspects 99
6.1.3 Remarks on the Absorbance Concept 102
6.2 The Effect of Planar Interfaces: Fresnel's Formulae 103
6.3 Total Reflection of Light 112
6.3.1 Conditions of Total Reflection 112
6.3.2 Discussion 113
6.3.3 Attenuated Total Reflection ATR 114

6.4 Metal Surfaces . . . 116
  6.4.1 Metallic Reflection . . . 116
  6.4.2 Propagating Surface Plasmon Polaritons. . . . 119
6.5 Anisotropic Materials . . . 125
  6.5.1 Interface Reflection Between an Isotropic and an Anisotropic Material . . . 125
  6.5.2 Giant Birefringent Optics . . . 128

7 Thick Slabs and Thin Films . . . 131
7.1 Transmittance and Reflectance of a Thick Slab. . . . 131
7.2 Thick Slabs and Thin Films . . . 136
7.3 Spectra of Thin Films . . . 139
7.4 Special Cases . . . 142
  7.4.1 Vanishing Damping . . . 142
  7.4.2 Halfwave Layers. . . . 144
  7.4.3 Quarterwave Layers . . . 145
  7.4.4 Free-Standing Films . . . 147
  7.4.5 A Single Thin Film on a Thick Substrate. . . . 149
  7.4.6 A Few More Words on Reverse Search Procedures . . . 153

8 Gradient Index Films and Multilayers . . . 163
8.1 Gradient Index Films. . . . 163
  8.1.1 General Assumptions. . . . 163
  8.1.2 *s*-Polarization . . . 166
  8.1.3 *p*-Polarization . . . 168
  8.1.4 Calculation of Transmittance and Reflectance. . . . 169
8.2 Multilayer Systems . . . 175
  8.2.1 The Characteristic Matrix. . . . 175
  8.2.2 Characteristic Matrix of a Single Homogeneous Film . . . 177
  8.2.3 Characteristic Matrix of a Film Stack . . . 177
  8.2.4 Calculation of Transmittance and Reflectance. . . . 178

9 Special Geometries . . . 181
9.1 Quarterwave Stacks and Derived Systems . . . 181
9.2 Chirped and Dispersive Mirrors . . . 185
  9.2.1 Basic Properties of Short Light Pulses: Qualitative Discussion. . . . 185
  9.2.2 General Idea of Chirped Mirror Design . . . 189
  9.2.3 First and Second Order Dispersion Theory. . . . 190
  9.2.4 Spectral Targets for Dispersive Mirrors and Examples. . . . 195
9.3 Structured Surfaces . . . 200

9.4 Remarks on Resonant Grating Waveguide Structures 202
9.4.1 General Idea 202
9.4.2 Propagating Modes and Grating Period 203
9.4.3 Energy Exchange Between the Propagating Modes . . . 205
9.4.4 Analytical Film Thickness Estimation for a GWS 206
9.4.5 Examples on GWS-Based Simple Reflector and Absorber Designs 208
9.5 Resume from Chaps. 6–8 and this Chapter 213
9.5.1 Overview on Main Results 213
9.5.2 Further Experimental Examples 215
9.5.3 Problems 220

Part III Semiclassical Description of the Interaction of Light with Matter

10 Einstein Coefficients 229
10.1 General Remarks 229
10.2 Phenomenological Description 230
10.3 Mathematical Treatment 232
10.4 Perturbation Theory of Quantum Transitions 233
10.5 Planck's Formula 239
10.5.1 Idea 239
10.5.2 Planck Distribution 240
10.5.3 Density of States 240
10.6 Expressions for Einstein Coefficients in the Dipole Approximation 243
10.7 Lasers 247
10.7.1 Population Inversion and Light Amplification 247
10.7.2 Feedback 248

11 Semiclassical Treatment of the Dielectric Function 255
11.1 First Suggestions 255
11.2 Calculation of the Dielectric Function by Means of the Density Matrix 257
11.2.1 The Interaction Picture 257
11.2.2 Introduction of the Density Matrix 258

12 Solid State Optics 271
12.1 Formal Treatment of the Dielectric Function of Crystals (Direct Transitions) 271
12.2 Joint Density of States 276
12.3 Indirect Transitions 281
12.4 Amorphous Solids 284
12.4.1 General Considerations 284

12.5 Resume from Chaps. 10–11 and this Chapter 292
12.5.1 Overview on Main Results. 292
12.5.2 Problems 295

Part IV Basics of Nonlinear Optics

13 Some Basic Effects of Nonlinear Optics 303
13.1 Nonlinear Susceptibilities: Phenomenological Approach. 303
13.1.1 General Idea. 303
13.1.2 Formal Treatment and Simple Second Order Nonlinear Optical Effects. 305
13.1.3 Some Third Order Effects 312
13.2 Calculation Scheme for Nonlinear Optical Susceptibilities 315
13.2.1 Macroscopic Susceptibilities and Microscopic Hyperpolarizabilities 315
13.2.2 Density Matrix Approach for Calculating Optical Hyperpolarizabilities 316
13.2.3 Discussion 321
13.3 Resume for this Chapter 325
13.3.1 Overview on Main Results. 325
13.3.2 Problems 327

14 Concluding Remarks 329

Too Many Equations?—A Very Final Remark on Physicists and Mathematics. 335

Bibliography 337

Index 347

Symbols and Abbreviations

A	Absorptance
A	Amplitude
A_j, a_j	Arbitrary expansion coefficients (in Chaps. 3 and 10)
$\boldsymbol{A}$	Operator in quantum mechanics
A_{21}	Einstein's coefficient for spontaneous emission
a	Sometimes used for geometrical dimensions (for example lattice constant, interatomic spacing, or others, as follows from the text)
a_0	Bohr's radius
α	Absorption coefficient
B_j, b_j	Arbitrary expansion coefficients (in Chap. 4)
$\boldsymbol{B}$	Magnetic induction
B_{21}	Einstein's coefficient for stimulated emission
B_{12}	Einstein's coefficient for absorption
β	Linear microscopic polarizability
β_h	Linear polarizability of the host
$\beta^{(j)}$	Polarizability of j-th order
C	Constant
c	Velocity of light in vacuum
$\boldsymbol{D}$	Electric displacement
D	Density/joint density of quantum states
d	Physical (film) thickness
d_{sub}	Physical substrate thickness
δ	Phase, phase shift
$\boldsymbol{E}$, E	Electric field strength
E_0	Field amplitude
E_0	Band gap (in Chap. 12)
E_g	Direct band gap
E_n	Energy level in quantum mechanics
$\boldsymbol{e}$	Unit vector
e	Basis of natural logarithm
ε_0	Permittivity of free space

ε	Dielectric function
ε’	Real part of the dielectric function
ε”	Imaginary part of the dielectric function
ε_{xx}	Diagonal element of the dielectric tensor
ε_h	Dielectric function of the host
ε_{stat}	Static value of the dielectric function
ε_∞	“Background” dielectric function (in Chap. 4)
F	Error function
f_j	Relative strength of the absorption lines
f_{ij}	Oscillator strength in quantum mechanics
φ	Angle of incidence; in Chaps. 1 and 13: zero-phase
φ_B	Brewsters angle
GBO	Giant Birefringent Optics
GWS	Grating waveguide structure
γ	Damping constant
Γ	Homogeneous linewidth
$\boldsymbol{H}$, H	Magnetic-field strength
$\boldsymbol{H}$	Hamilton operator, Hamiltonian
H	Quarterwave layer with high refractive index (in Chap. 9)
HW	Halfwave
I	Intensity
IR	Infrared spectral region
i	Counting index (in sums, in quantum mechanics)
i	Imaginary unit
$\boldsymbol{j}$	Electric current density
j	Counting index (in sums, in quantum mechanics)
K	Extinction coefficient
$\boldsymbol{K}$	Wave vector
k	Counting index (in sums, in quantum mechanics)
κ	Response function
k_B	Boltzmann’s constant
L	Depolarisation factor (Chaps. 3 and 4)
L	Optical loss (in Chap. 6)
L	Quarterwave layer with low refractive index (in Chap. 9)
l	Counting index (in sums, in quantum mechanics)
l, L	Sometimes used for geometrical dimensions
LO	Linear optics
λ	Wavelength in vacuum
Λ	Period of a diffraction grating
$\boldsymbol{M}$	Magnetization
M	Number
$\hat{\boldsymbol{M}}$	Characteristic matrix
m_{ij}	Matrix elements
m	Mass

m	Counting index (in sums, in quantum mechanics)
μ_0	Permeability of free space
MIR	Middle infrared spectral region
N	Concentration
N	Number (where specified)
n	Counting index (in sums, in quantum mechanics)
n, n_0	Refractive index
n_{sub}	Substrate refractive index
$n_{(e,\mathrm{o})}$	Extraordinary or ordinary refractive index in Chap. 6
n_v	Refractive index of the void material
$\hat{n}$	Complex index of refraction
NIR	Near infrared spectral region
NLO	Nonlinear optics
θ	Step function
p	Dipole moment
p_j	Filling factor
$\boldsymbol{P}$, P	Polarization
PIAD	Plasma ion assisted evaporation
$P^{(j)}$	Polarization of j-th order
$\boldsymbol{p}_{ml}$	Matrix element of the dipole operator
ψ	Refraction angle, propagation angle
ψ	Time-independent wavefunction in quantum mechanics
Ψ	Time-dependent wavefunction in quantum mechanics
q	Charge
QW	Quarterwave
R	Radius
R	Reflectance
R_p	Reflectance of p-polarized light
R_s	Reflectance of s-polarized light
$\boldsymbol{r}$	Position vector with $\mathbf{r} = (\mathrm{x}, \mathrm{y}, \mathrm{z})^{\mathrm{T}}$
$r_{(s,p)}$	Field reflection coefficient (for s- or p-polarized light)
ρ	Mass density
$\boldsymbol{\rho}$	Density matrix in a mixed quantum state
ρ_{nm}	Elements of the density matrix
S	Scatter
σ	Conductivity
σ	Standard deviation in a Gaussian distribution
σ_{stat}	Static value for the conductivity
$\boldsymbol{\sigma}$	Density matrix of a pure quantum state
σ_{nm}	Elements of the density matrix
T	Absolute temperature
T	Transmittance
t	Field transmission coefficient
t	Groove depth (Chap. 9)
t	Time

t_{coh}	Coherence time
τ	Time constant, relaxation time, pulse width
u	Spectral density
UV	Ultraviolet spectral region
$\boldsymbol{V}$	Perturbation operator
V	Volume
V_j	Fraction volume
V_{ij}	Matrix element of the perturbation operator
v_{phase}	Phase velocity
v_z	z-component of the velocity
ν	Wavenumber
VIS	Visible spectral region
VP	Cauchy's principal value of the integral
W	Probability
w	Relative weight function
w	Boltzmann's factor in Chap. 10
ω	Angular frequency
ω_0	Eigenfrequency, resonance frequency
ω_D	Doppler-shifted frequency
ω_p	Plasma frequency
$\tilde{\omega}_0$	Shifted with respect to local field effects resonance frequency
ω_{nm}	Transition frequency, resonance frequency in quantum mechanics
$\Delta\omega$	Spectral bandwidth
x	Position
χ	Linear dielectric susceptibility
χ_h	Linear dielectric susceptibility of the host
χ_{stat}	Static value of the susceptibility
χ_{res}	Resonant contribution to the susceptibility
χ_{nr}	Nonresonant contribution to the susceptibility
$\chi^{(j)}$	Susceptibility of j-th order
Z	Number of quantum states

Chapter 1
Introduction

Abstract The topic of thin film optics/thin film optical spectroscopy can be tackled as a particular case of a broader class of phenomena, concerned with the interaction of electromagnetic irradiation with matter. A grammar description of this class of phenomena requires detailed analysis of the specific effects arising from material properties, as well as from the particular sample geometry. The analysis may be performed on both classical and quantum mechanical levels of description.

1.1 General Remarks

Whenever one is involved in spectroscopic experiments with electromagnetic waves, knowledge on the interaction of electromagnetic irradiation with matter is in the fundament of the theoretical understanding of the experimental results. This is true, for example, in molecular as well as in solid state optical spectroscopy. The light-with-matter interaction is the basis of numerous analytical measurement methods, which are applied in physics as well as in chemistry and biology. There is a tremendous amount of scientific publications and textbooks which deal with this subject. So what was the reason for writing this book?

The main reason was that in the present monograph the subject is described from the specific viewpoint of the *thin film spectroscopist*, and not from the viewpoint of general solid state or molecular optical spectroscopy. Caused by the specific geometry of a thin film sample, in thin film spectroscopy one needs a substantially modified mathematical description compared to the spectroscopy of other objects. The reason is that a thin film has a thickness that is usually in the nanometer- or micrometer region, while it may be considered to extend to infinity in the other two (lateral) dimensions. Of course, there also exist monographs on thin film optics (and particularly on optical coatings design). It is nevertheless the experience of the author that there appears to be a discrepancy between the typical reader's knowledge on the subject and the scientific level that is presumed to understand the highly specialized scientific literature. Moreover, the interaction of light with matter is

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usually not teached as a separate university course. An interested student must therefore complete his knowledge referring to different courses or textbooks, such as those on general optics, classical continuum electrodynamics, quantum mechanics and solid state physics.

It is therefore the authors aim to provide the reader with a short and compact treatment of the interaction of light with matter (within an approach that is adapted to the specifics of thin solid films), and thus to bridge the gap between the readers basic knowledge on electrodynamics and quantum mechanics and the highly specialized literature on thin film optics and spectroscopy.

1.2 To the Content of the Book

In most practical cases, a thin film is built from a solid material. Therefore, the particular treatment in this book will mostly concern the specifics of the spectroscopy of solid matter. However, there appear situations where a general spectroscopic principle is easier to be explained referring to other states of matter. Inhomogeneous broadening of spectral lines is a typical example, as it is most easily explained in terms of the Doppler broadening as observed in gases. In such cases, we will happily leave the solid state specifics and turn to gases, in order to make the general principle more transparent.

Crystalline solids may be optically anisotropic. It is absolutely clear that a general and strong treatment of solid state spectroscopy must consider anisotropy. Nevertheless, in this book we will mostly restrict on optically isotropic materials. There are several reasons for this. First of all, many physical principles relevant in spectroscopy may be understood basing on the mathematically more simple treatment of isotropic materials. This is particularly true for many optical coatings, in fact, in optical coatings practice it is in most cases sufficient to work with isotropic layers models. There are exclusions from this rule, and in these situations anisotropy will be taken into account. This concerns, for example, the Giant Birefringent Optics (GBO) effects treated in connection with Fresnel's equations (Chap. 6). We will also refer to material anisotropy when discussing nonlinear optical effects at the end of this book (Chap. 13). By the way, the depolarization factors introduced in the first part of this book allow to a certain extent calculating the anisotropy in optical material constants as caused by the materials morphology (Chaps. 3 and 4). However, this book does definitely not deal with specifics of *wave propagation* in anisotropic materials.

Having clarified these general points, let us turn to the overall structure of this book. First of all it should be clear, that the reader is presumed to have certain knowledge on general optics, electrodynamics and quantum mechanics. It is not the purpose of this book to discuss the transversality of electromagnetic waves, nor to introduce the terms of linear or elliptical light polarization. The reader should be familiar with such kind of basic knowledge, as well as simple fundamentals of thermodynamics such as Boltzmann's and Maxwell's statistics.

Basing on this knowledge, the first part of the book (Chaps. 2–5) deals with the classical treatment of optical constants. In that classical treatment, both the electromagnetic field and the material systems will be described in terms of classical (non-quantum mechanical) models. Basing on Maxwell's equations, we will start with a rather formal introduction of optical constants and their frequency dependence (dispersion). We will have to introduce such important terms like the susceptibility, the polarizability, the dielectric function and the complex refractive index. We will then derive the main classical dispersion models (Debye-, Drude-, and the Lorentzian oscillator model). Starting from the Lorentz-Lorenz-formula, there will be a broad discussion of the optical properties of material mixtures. The first part of this book will be finished by the derivation of the Kramers-Kronig-relations for the dielectric function.

The second part (Chaps. 6–9) describes wave propagation in thin film systems. We start from Fresnel's equations for transmission and reflection at a single interface. This is an utmost important matter in thin film optics. For that reason, the discussion of these equations will fill up the full Chap. 6. In order to emphasize the physical value of these equations, we will derive a variety of optical and spectroscopic effects from them. Namely, this chapter will discuss Brewster's angle, total and attenuated total reflection of light, metallic reflection, propagating surface plasmon polaritons and the already mentioned GBO effects. In Chap. 7, the reader becomes familiar with the optical properties of thick slabs and single thin films. Chapter 8 deals with gradient index layers and film stacks; in particular, the matrix method for calculating transmittance and reflectance of an optical coating is introduced. In Chap. 9, some special cases are discussed, such as simple quarter-wave stacks, chirped mirrors, and the so-called grating waveguide structures.

The third part of the book (Chaps. 10–12) deals with the semiclassical treatment of optical constants. In this approach, the electromagnetic field is still described by Maxwell's equations, while the material system is described in terms of Schrödinger's equation. The goal is to obtain a semiclassical expression for the dielectric function, and consequently for the optical constants. Again, the reader is presumed to be familiar with basic knowledge on quantum mechanics and solid state physics, such as general properties of the wavefunction, simple models like the harmonic oscillator, perturbation theory, and Bloch waves. We start from the derivation of Einstein coefficients (Chap. 10). As a side effect of this derivation, we become familiar with quantum mechanical selection rules and Planck's formula for blackbody irradiation. By the way, we get the knowledge necessary to understand how a laser works. In Chap. 11, a density matrix approach will be presented to derive a general semiclassical expression for the dielectric polarizability of a quantum system with discrete energy levels. In Chap. 12, the derived apparatus will be generalized to the description of the optical constants of solids.

Finally, Chap. 13 (which forms the very short fourth part of the book) will deal with simple effects of nonlinear optics.

1.3 The General Problem

The basic problem we have to regard is the interaction of electromagnetic irradiation (light) with a specific kind of matter (a thin film system). In order to keep the treatment compact and "simple", we will restrict our discussion to the electric dipole interaction. We will assume throughout this book, that among all terms in the multipole expansion of the electromagnetic field, the electric dipole contribution is the dominant one, and that other (higher order electric and all magnetic) terms may be neglected.

It is also worth emphasizing, that this book does definitely not deal with optical coatings design. It rather pursues the physical understanding of the information that may be drawn from a thin film spectrum as obtained from the experiment. We will therefore start from the experimental situation a thin film spectroscopist is confronted with.

In the frames of classical electrodynamics, any kind of light (which is used in optics) may be regarded as a superposition of electromagnetic waves. The idea of optical spectroscopy (or in more general optical characterization) is quite simple: If we have an object to be investigated (we will call it a *sample*), we have to bring it into interaction with electromagnetic waves (light). As the result of the interaction with the sample, certain properties of the light will be modified. The specific modification of the properties of electromagnetic waves resulting from the interaction with the sample shall give us information about the nature of the sample of interest.

For sufficiently low light intensities, the interaction process does not result in sample damage. Therefore, the majority of optical characterization techniques belong to the non-destructive analytical tools in materials science. This is one of the advantages of optical methods.

Although the main idea of optical characterization is quite simple, it may be an involved task to turn it into practice. In fact one has to solve two problems. The first one is of entirely experimental nature: The modifications in the light properties (which represent our *signal*) must be detected experimentally. For standard tasks, this part of the problem may be solved with the help of commercially available equipment. The second part is more closely related to modelling: From the signal (which may be simply a curve in a diagram) one has to conclude on concrete quantities characteristic for the sample. Despite of the researcher's intuition and ability to identify or develop suitable models, this part may include severe computational efforts. Thus, the solution of the full problem requires the researcher to be skilled in experiment and theory (even mathematics) alike.

Let us now have a look at Fig. 1.1. Imagine the very simplest case—a monochromatic plane light wave impinging on a sample which is to be investigated. Due to the restriction on electric dipole interaction, we will only discuss the electric field of the light wave. In a complex notation, it may be written according to:

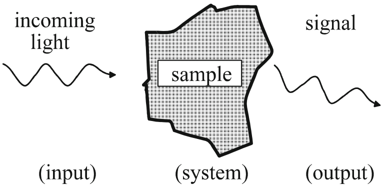

Fig. 1.1 Optical signal as the result of interaction of an electromagnetic wave with the sample

$$\boldsymbol{E} = \boldsymbol{E}(\boldsymbol{t}, \boldsymbol{r}) = \boldsymbol{E_0 e}^{-i(\omega t - \boldsymbol{kr})} \tag{1.1}$$

The parameters characterizing the incoming light (angular frequency ω, intensity (depends on the amplitude $\boldsymbol{E}_0$), polarization of the light (direction of $\boldsymbol{E}_0$), propagation direction (direction of $\boldsymbol{k}$)) are supposed to be known. Imagine further, that as the result of the interaction with the sample, we are able to detect an electromagnetic wave with modified properties. Which properties of the electromagnetic wave may have changed as the result of the interaction with the sample?

In principle, all of them may have changed. It is absolutely possible, that the interaction with the sample leads to changes in the frequency of the light. Typical examples are provided by Raman Scattering, or by several nonlinear optical processes. The polarization direction of the light may change as well. Ellipsometric techniques detect polarization changes and use them to judge the sample properties. Clearly, the light intensity may change (in most cases the light will be attenuated). This gives rise to numerous photometric methods analysing the sample properties basing on the measurement of intensity changes. And finally, anybody knows that the refraction of light may lead to changes in the propagation direction. Any refractometer makes use of this effect to determine the refractive index of a sample.

So we see, that the diversity of parameters characterizing electromagnetic radiation (in practice they are more than those mentioned here) may give rise to quite diverse optical characterization techniques.

We have now formulated our task: Starting from the analysis of certain parameters of the electromagnetic irradiation after having interacted with the sample, we want to obtain knowledge about the properties of the sample itself. Which kind of sample properties may be accessible to us?

Shortly spoken, the electromagnetic wave coming from the sample carries information about both the *sample material* and *sample geometry* (and the experimental geometry, but the latter is usually known to us). And if one is interested in the pure material properties, the geometrical influences on the signal have to be eliminated—experimentally or by calculations. In worse cases (and thin film spectra belong to these worse cases), geometrical and material informations are intermixed in the spectrum in a very complicated manner. In thin film systems, this is caused by the coherent superposition of electric fields arising from multiple internal reflections of light at the individual film interfaces. An experimental elimination of the geometrical sample contributions is then usually impossible, so that the derivation of material properties often becomes interconnected with the instantaneous derivation of the geometrical properties by a corresponding mathematical treatment. As the result, we obtain information about both the sample material properties (for example the refractive index) and the geometry (for example the film thickness).

In order to make the theoretical treatment of thin film spectra more understandable, we will therefore develop the theory in two subsequent steps. The first step deals with the description of pure material parameters, such as the refractive index, the absorption coefficient, the static dielectric constant and so on. We will present several models that describe these parameters in different relevant physical systems.

The second step will be to solve Maxwell's equations in a system with given material parameters and a given geometry. In our particular case, we will do that for thin film systems. As the result, we obtain the electric field of the wave when it has left the system. Its properties will depend on the systems material *and* geometry. Having calculated the electric field, all the signal characteristics mentioned before may be theoretically derived. In the present book, the treatment will follow this philosophy.

In spectroscopy practice, one will proceed in a similar manner. The theoretical analysis of a measured spectrum starts from a hypothesis on the sample properties, including its material properties and geometry. Then, Maxwell's equations are solved, and the calculated characteristics are compared to the experimental values. From that, one may judge whether or not the assumptions previously made on the system were reasonable. If not, the assumed sample properties have to be altered, until a satisfying agreement between experiment and theory is achieved.

1.4 One Remark Concerning Conventions

Let us make an important remark concerning a convention implicitly made when writing down (1.1). Of course, the natural writing of the electric field in a monochromatic plane wave would operate with real functions and coefficients only. For such real fields, we could use a description of the type:

$$E_{real}(t,\boldsymbol{r}) = E_{0,real}\cos(\omega t - \boldsymbol{kr} + \varphi) \tag{1.2}$$

However, the cosine function appears to be quite inconvenient with respect to our further mathematical treatment. On the other hand, it can be written as:

$$E_{real}(t,\boldsymbol{r}) = \frac{1}{2}\left[E_{0,real}e^{-i(\omega t-\boldsymbol{kr})}e^{-i\varphi} + E_{0,real}e^{i(\omega t-\boldsymbol{kr})}e^{i\varphi}\right] \equiv E_0 e^{-i(\omega t-\boldsymbol{kr})} + c.c \tag{1.3}$$

Here “c.c.” denotes the conjugate complex to the preceding expression. It turns out, that the initially real electric field may be expressed as the sum of a complex field and its conjugate complex counterpart, while the latter does not contain any new physical information. Hereby, we have introduced the complex field amplitude E_0 as:

$$E_0 \equiv \frac{E_{0,real} e^{-i\varphi}}{2} \tag{1.4}$$

In practice, it appears much more convenient to build the further theory using complex electric fields $E(t, \boldsymbol{r})$ according to (1.3) and (1.4) instead of working with the real version (1.2). Therefore, in our treatment we make use of the complex field defined by (1.1), keeping in mind that the initially real field will be obtained when adding the complex conjugate to (1.1). Or, in other words:

$$E_{real}(t, \boldsymbol{r}) = 2\mathrm{Re}E(t, \boldsymbol{r}) \tag{1.5}$$

where $E(t, \boldsymbol{r})$ is given by (1.1) and (1.4). But the choice of (1.1) for the complex writing of the electric field defines a particular convention, which is used throughout this book. When looking at (1.3), it becomes evident that we could have used the writing:

$$E_{real}(t, \boldsymbol{r}) = \frac{1}{2}\left[E_{0,real} e^{+i(\omega t - \boldsymbol{kr})} e^{+i\varphi} + E_{0,real} e^{-i(\omega t - \boldsymbol{kr})} e^{-i\varphi}\right] \equiv E_0 e^{+i(\omega t - \boldsymbol{kr})} + c.c;$$
$$E_0 \equiv \frac{E_{0,real} e^{+i\varphi}}{2}$$

as well. It makes absolutely no physical difference whether, in (1.1), the plus or minus sign is chosen in the exponent. These are only two different conventions. But once we have decided on one of these conventions, we should strictly adhere to it in the following, in order to avoid convention confusion. In our particular treatment, we will use the minus-sign as fixed in (1.1). In other sources, the other convention may be used, which results in differences in the equations to be derived in the following.

Having clarified the general features of our approach, let us now turn to the introduction of the linear optical susceptibility.