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Olaf Stenzel

Optical Coatings

Material Aspects in Theory and Practice

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Optical Coatings

Material Aspects in Theory and Practice

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To Gabi



View inside a coating deposition chamber equipped with in situ optical monitoring system OptiMon

Foreword

This is the book that I wish I had had years ago. The optical coating pioneer Francis Turner once told me that in the very early days of optical coatings he and other workers really thought that thin solid films was a correct and sufficient description of the layers in their coatings. We have learned a lot since then, and especially that mastery of our materials is the vital prerequisite for mastery of our optical coatings. It has been a hard lesson, and, indeed, we are still learning. Experience is an excellent though rather slow and often bitter teacher. But where can we find a better one? We need look no further than the author of this book. Of course, there is always the primary literature. But that is scattered, and, invariably, assumes knowledge of what has gone before, and is created by multiple authors with multiple styles. For efficient learning we need a single author who takes the trouble to start from the beginning and to explain, in as simple terms as possible, what is an exceedingly complex and difficult collection of phenomena. Such a coherent, connected description has been lacking—until now. We all use mathematics as our most powerful descriptive tool. It provides us with an unmatched predictive capacity, but, on its own it is not always the best tool for understanding. Understanding is what is most important, and, once achieved, the analysis then follows naturally. That approach is the thrust of this book, which concentrates on understanding. It begins by pointing out a simple but neglected fact that becomes completely obvious once explained. Unlike most other forms of material, a thin film is dominated by its surface. [Chapter 1](#) of the book, alone, should be required reading for anyone entering the field of optical coatings.

All of us who have spent even the shortest time in optical coatings have surely gained some experience. Observed effects can sometimes be rather strange, and in the old days were often thought to be a matter of luck, and the pursuit of optical coatings was often described, not altogether in jest, as a black art. The problems, of course, had nothing to do with luck or magic but were symptoms of the complex nature of the films and the lack of a logical framework in which to set the products of experience. Here is the framework, in all its logical detail, as the subject of this book. We are led through the ideas of the fundamental optical properties of materials and how they are influenced by their atomic and molecular arrangements and by their microstructure. Various models of their behavior are introduced and extended to mixtures of materials that present still further structural features. Enough is included on the various classes of optical coatings that it is not

necessary to read the book in conjunction with other material. Then the properties of certain specific materials of great importance in optical coatings are described. Materials with an intentional lateral structure, different in scale from their atomic structure, are currently increasing in importance in optical coatings and here we find what has to be the most understandable introduction to them. I can describe the whole book chapter by chapter, but you must read it for yourself.

The book can be treated as a reference. The chapters are largely self-standing so that they can be read separately, but my own experience was that once I started to read the book I found it difficult to put it down. It reads naturally from cover to cover. Once read, this is a book to be kept on the shelf nearest my hand.

Tucson

Angus Macleod

Preface

About this Book

*“Auch schien’s ihm höchst verwundersam,
Wenn jemand mit der Lampe kam,
Er staunt, er glotzt, er schaut verquer,
Folgt der Erscheinung hin und her
Und weidet sich am Lichteffect.
Man sieht bereits, was in ihm steckt.”*

*(engl. “It further seemed to him most strange
When there a lamp came in his range
Of vision. Looking, blinking, staring
He follows the apparition glaring
And feast on the effect of light.
Thus are his gifts revealed all right.”)*

About the baby-Maler Klecksel, in Wilhelm Busch: Maler Klecksel (engl. Klecksel the Painter), (1884), Translation from German by Laureate of Nobel Prize in Physics 1954, Max Born (!)

Dear interested reader,

It is my pleasure to realize that you hold this book in your hands or maybe read this Preface at the website of Springer Publishing or your book dealer. You know that optics represents a fascinating subchapter of physics, and it is hard to describe the natural fascination arising from optical phenomena more convincing than done by Wilhelm Busch in the above given citation. But maybe you have not yet known that nobody other than Max Born performed the translation of that nice illustrated story into the English language [1]—I learned that only in the course of writing this book.

I do not know how many thousand books have been written on optical topics, but nevertheless at the moment you are reading this particular Preface. I would therefore like to use it to give you some information about the background motivation and purpose of this book, which might facilitate your decision on whether or not to read it.

First of all I would like to give you some information about the predecessors of this book. It was 18 years ago that I wrote a German textbook which was

published in 1996 with the title “Das Dünnschichtspektrum: Ein Zugang von den Grundlagen zur Spezialliteratur” (The thin film spectrum: from basics to specialized literature) with Akademie Verlag GmbH, Berlin. That first book has 190 pages crammed with derivations and equations, while the material selection was strongly influenced by the always individual experience on supervising and working with students. The emphasis of that book was definitely on the formal theoretical treatment of the optical response of thin solid films, the pursued audience was composed from German-speaking master and Ph.D. students of relevant topics.

Nine years later, it was my pleasure to collaborate for the first time with Claus Ascheron, Springer-Verlag Berlin Heidelberg, with a new book project, this time in English language. The result appeared in 2005 with the title: “The physics of thin film optical spectra: An introduction.” It has already 275 pages comprising to a certain extent the formal treatment from the first book, but enriched with more applicative aspects. It is again a typical textbook where everything is derived starting from Maxwells or Schrödingers Equations, and at present it is the textbook to the university course “Thin Film Optics,” which is given for Master of Photonics students at Friedrich-Schiller-University Jena, Institute of Applied Physics, Abbe Center of Photonics.

And now, again 9 years later, this new book appears. It is rather a complement to its predecessors, with another focus, and it is pursuing a somewhat broader audience. In contrast to its predecessors, it is not a textbook that could be in the basis of a university lecture course. In essence, it is based on materials that I have presented in various short courses aimed at further advanced professional training and qualification in a rather condensed manner. These short courses have been held in the frames of several Optical Interference Coating (OIC) conferences, as well as substantial part of applied optics professional network training workshops (Optence and OTTI, Germany). In such courses, practically no derivation of equations is provided, but the focus is rather on practical examples. Hence, a lot of experimental data are presented, sometimes combined with intuitive and illustrative approaches as well as with diverse “rules of thumb” and “quick and dirty” methods for data evaluation. It was my intention to condense this store of knowledge into a further book text while completing it with a few introductory chapters containing the essence of the standard background material, as well as some considerations on the relevance of the underlying model assumptions. Concerning the latter, it is in fact not so easy to find generally accepted and at the same time consistent treatments in the literature. Therefore (and this primarily concerns [Chaps. 3 and 4](#)), the discussion of the relevance of the physical models rather represents the personal view of the author of this book, which is not necessarily shared by all of my colleagues in the field.

Finally, some additional chapters on nanostructured and mixture coatings have been included. Also, the material from two tutorial texts, which I authored or co-authored by invitation of the Journal “Advanced Optical Technologies,” has completed the content of this book.

Thus, in this book, only few derivations are given, and when they are really necessary, they are (in most cases) exported into some appendices. Practically all

derivations concerning the basic chapters are given in [2], and therefore, *practically nothing is rederived* in this text. In this sense, this new book is a complement to the preceding one. A reader interested in the derivation of a certain equation is kindly referred to [2] or another thin film textbook. But the book can also be read without referring to other sources, when knowledge about the concrete origin of the equations is not of interest.

Furthermore, the present book is neither an introduction into thin film optics/thin film design nor a reference book on optical constants in its verbal meaning. These books already exist (see the introduction [Chap. 1](#)); and with respect to tables of optical constants, you are kindly referred to [3]. The present book is rather intended to develop a classical and sometimes illustrative physical picture of the origin and correlation between different coating material properties, and of how the knowledge on these correlations can be used in coating theory and practice, including oxide, fluoride, metal and organic coatings, as well as mixed and nanostructured coating materials. Quantum mechanical treatments are avoided, whenever possible.

One might question the sense of such an approach referring to the highly developed theoretical formalism of quantum mechanics, which supplies us with algorithms to calculate practically everything, whenever a suitable Hamiltonian may be formulated. So what might be the sense of applying these old but simple classical approaches today?

The answer is not so much related to their simplicity. Instead, what classical physics does is to supply us with vital pictures on what might happen in reality when the process described by a certain equation would be initiated in practice. It is that appeal to the power of a physicist's imagination, which turns classical models into powerful heuristic tools in physics. And it is my pleasure to refer in this context to the Preface of a book written by the highly appreciated surface and coating spectroscopy expert Peter Grosse [4], where this argumentation is developed with respect to today's use of applying the Drude theory throughout a full book text.

Once my first book had 190 pages and the second one 275 pages, I felt some obligation to continue (and finish) this series with a $275 \times 275/190$ pages volume, i.e., approximately 400 pages. While completing this manuscript, I feel that the volume which you hold in hand or have on your screen comes close to this goal.

One more remark on history: when looking into classical literature, but also into modern novellas, you will be astonished about the multiplicity of literal reflections about physical and optical phenomena. The texts of Johann Wolfgang von Goethe, Wilhelm Busch, E. T. A. Hoffmann, and others contain plenty of hidden allusions to physical and optical phenomena, as well as to spectacular scientific observations which have been made in their times. Some of them even fall close to modern optical coating problems, such as the disappearance of human's mirror image in Hoffmann's ingenious story "The lost reflection." Of course, the magician Dapertutto is definitely not a coating scientist, but nevertheless the formulated reflection target is challenging even today, and I like to refer to it as the Dapertutto's antireflection problem.

While highly appreciating the creative ideas of these authors, I decided to start each of the chapters of this book with a (literature) citation that seemed suitable for introducing into the particular topic. Despite the already mentioned authors, interesting material can be found in texts of Edgar Allan Poe, John Ronald Reuel Tolkien, Stephen King, and others. I hope you can read this small collection of citations with some feeling of enjoyment, but in the case that you are a lecturer as I am, maybe you find some of them helpful and stimulating for further use in your own courses.

As one of the purposes of this book was to illustrate the validity of certain correlations by publicly available experimental material, I had to make extensive use of literature sources where the necessary data are tabulated. The reference to the original material is usually included directly into the text or into the figure captions. All references are then collected in the references section at the end of the corresponding chapter. Some of the sources appeared to be websites; I understand that they may no more be available at the moment when you read this book, but practically those references reflect what was available on the Internet in the year 2012.

There are so many people who gave me assistance and (sometimes even involuntary) stimulation to write this book, that I decided to export the acknowledgments into a separate subchapter. So that for the moment let me thank you for your interest and express my hope that you are biased enough now to proceed reading by switching to the introduction chapter.

With my best wishes

Acknowledgments

It was a good piece of work, but nevertheless it appeared straightforward to give a survey on simple classical models applicable to the phenomena observed in thin solid films. But as soon as any practically relevant theory is to be supported or falsified by experimental data, it appeared necessary to complete the text with comprehensive experimental material. The latter had been collected over the latest decade with the help of plenty of colleagues and collaborators, and it is impossible to mention all of them here. Instead, I would like to express my thanks rather *en masse* to the consortia of the projects IntIon, nanomorph, TACo, TAILOR, and PluTO, and to acknowledge the support by the sponsoring ministries—the BMWi, the BMWA, and the BMBF in Germany. More concrete data on collaborators and companies/institutions are found in the relevant author lists and acknowledgments of the cited references, where all of these data have been originally published prior to the writing of this book.

I am very grateful to Johannes Ebert (Laseroptik GmbH), Thomas Köhler (*Bremen Center for Computational Materials Science BCCMS*), Todd Perkins (Kaiser Optical Systems, Inc.), and Bettina Loycke (Wiley-VCH Verlag GmbH & Co. KGaA) for the supply of specific pictures and the permissions to reproduce

them in this monograph. Plenty of material used in this book has been generated during project work at Fraunhofer IOF, and it is my pleasure to thank Norbert Kaiser for the permission to include corresponding experimental results into this monograph, as well as Torsten Feigl, Hagen Pauer, Ulrike Schulz, Kevin Füchsel, Astrid Bingel, and Steffen Wilbrandt for supplying me with corresponding graphical material.

The add-on for calculating the performance of gradient layers and rugate filters (Chaps. 4, 9, and 10) has been created by Tatjana Amotchkina (at that time Moscow State University). Data on aluminum–oxifluoride coatings produced by IBS (Chap. 11) have kindly been provided by Henrik Ehlers (Laser Zentrum Hannover). ITO and aluminum samples used for demonstration purposes in Chap. 5 have been provided by Daniel Gäbler (X-FAB Semiconductor Foundries AG). Their contributions were extremely helpful to complete the database which is in the background of this book with external material.

Steffen Wilbrandt performed a proofreading of Chap. 5. Rebecca Sequeira Schäffer (IOF) was able to organize absolutely every reference from the literature in the shortest time. Dieter Gäbler kindly supplied me with special material on aluminum hydroxide modifications.

Technical assistance in figure and manuscript preparation was provided by Josephine Wolf, Matthias Böhme, Johannes Gäbler, and Steffen Wilbrandt (all from IOF in Jena). The photograph in the title page was also taken by Johannes Gäbler.

I would like to express my special thanks to all of the mentioned persons.

Let me finally express my deepest gratitude to Prof. Angus Macleod, who quickly recognized the deepest intentions I had when planning and writing this book, and condensed them into a tailored and valuable Foreword, at the same time putting the book into the correct context with respect to the broader field of coating science.

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Symbols and Acronyms

a	Parameter in the Morse potential
A	Absorptance
\mathcal{A}	Potential absorptance
A	In Appendix B: wave amplitude
AFM	Atomic Force Microscopy
ALD	Atomic Layer Deposition
AP	Assistance parameter
APS	Advanced Plasma Source
$A, a_{(j)}$	Arbitrary coefficients (in Chap. 2)
a_{LJ}	Parameter in the Lennard Jones potential
α	Absorption coefficient
b	Fitting parameter in Appendix C
B	Arbitrary coefficient (in Chap. 2)
b_{LJ}	Parameter in the Lennard Jones potential
BIAS	Bias voltage
BP	Bragg Pippard
BR	Bragg Reflector
β	Linear microscopic polarizability
β	Absorptive part of EUV index of refraction
C	Arbitrary coefficient (in Chap. 2)
c	Velocity of light in vacuum
CME	Computational manufacturing experiment
CRW	Central rejection wavelength
CVD	Chemical Vapor Deposition
D	Diameter
DF	Dielectric function
DF	Discrepancy function
DIBS	Dual Ion Beam Sputtering
DUV	Deep ultraviolet spectral range
d	Physical (film) thickness
d_{sim}	Simulated film thickness
d_{sub}	Physical substrate thickness
d_{tar}	Target film thickness

δ	Phase, phase shift
δ	Refractive part of EUV index of refraction
E, E	Electric field strength
EBE	Electron Beam Evaporation
EMA	Effective medium approximation
EUV	Extreme ultraviolet spectral region
E_0	Field amplitude
E_{04}	Band gap defined through a threshold absorption level
E_{gap}	Band gap, general
E_{Tauc}	Tauc gap
E_n	Energy level in quantum mechanics
e	Unit vector
e	Basis of natural logarithm
ϵ_0	Permittivity of free space
ϵ	Dielectric function
ϵ_h	Dielectric function of the host material
ϵ_{stat}	Static value of the dielectric function
f_j	Relative strength of the absorption lines
f_{nl}	Oscillator strength in quantum mechanics
φ	Incident angle
φ_B	Brewsters angle
G	Reciprocal grating vector
GWS	Grating waveguide structure
γ	Damping constant
Γ	Homogeneous linewidth
H	Hamilton operator, Hamiltonian
H	QW layer with high refractive index
HR	High reflector
HW	Halfwave
h	Height
I	Intensity
i	Imaginary unit $i \equiv (0, 1)$
i	Counting index in sums
IAD	Ion Assisted Deposition
IBS	Ion Beam Sputtering
IP	Ion Plating
IR	Infrared spectral region
ITO	Indium tin oxide
j	Counting index in sums
k	Extinction coefficient
k	Wave vector
KK	Kramers–Kronig
L	Depolarization factor
L	Optical loss

L	Number of spectra in Sect. 5.7
L	QW layer with low refractive index
l	Counting index (in sums, in quantum mechanics)
l, L	Sometimes used for geometrical dimensions
LIDT	Laser-induced damage threshold
LL	Lorentz Lorenz
λ	Wavelength in vacuum
λ_c	Cutoff wavelength
Λ	Spatial period
\hat{M}	Characteristic matrix
m	Counting index (in quantum mechanics)
m	Mass
m_{core}	Mass of an atomic core
m_e	Electron mass
m_N	Mass of energetic gas atom incident during a film deposition process
m_p	Mass of a nucleon
MF	Merit function
MeF	Metal fluoride
MG	Maxwell Garnett
MIR	Middle infrared spectral region
MS	Magnetron Sputtering
N	Concentration
N	Number (of periods, layers, spectral points, or the like)
N_A	Number of atomic cores in a molecule
n	Counting index (in sums, in quantum mechanics)
n, n_j	Refractive index
n_{sub}	Substrate refractive index
\hat{n}	Complex index of refraction
NBP	Narrow Bandpass Filter
NIR	Near infrared spectral region
ν	Wavenumber
ν_d	Abbe number
OLED	Organic light emitting diode
OTTI	Ostbayerisches Technologietransferinstitut e.V.
p	Dipole moment
p	Porosity
p_j	Filling factor
p_M	Filling factor of the metal fraction
p_{solid}	Packing density
\mathbf{P}, P	Polarization
PARMS	Plasma Assisted Reactive Magnetron Sputtering
PIAD	Plasma Ion Assisted Deposition
PLD	Pulsed Laser Deposition
PTCDA	3,4:9,10-Perylenetetracarboxylic dianhydride

PTCDI	3,4:9,10-Perylenetetracarboxylic diimide
PVD	Physical Vapor Deposition
p_{mi}	Matrix element of the dipole operator
ψ	Refraction angle, propagation angle
ψ	Time-independent wavefunction in quantum mechanics (Appendix D)
Ψ	Potential transmittance
q	Electric charge
QW	Quarterwave
R	Radius, pore radius
R	Reflectance
R_p	Reflectance of p-polarized light
R_s	Reflectance of s-polarized light
\mathbf{r}	Position vector with $\mathbf{r} = (x, y, z)^T$
$r_{(s,p)}$	Field reflection coefficient (for s- or p-polarized light)
ρ	Mass density
ρ	Ratio of field reflection coefficients (in ellipsometry)
ρ_{nm}	Elements of the density matrix
$\rho_{ll}^{(0)}$	Unperturbed diagonal elements of the density matrix (population of l -th quantum level in thermodynamic equilibrium): $\rho_{ll}^{(0)} = W(l)$
s	Spacer order
S	Surface area
S	Scatter loss
S_R	Back scatter loss
S_T	Forward scatter loss
sccm	Standard cubic centimeters
SEM	Scanning Electron Microscopy
σ	Standard deviation, electric conductivity, surface roughness
σ_{large}	Large-scale root mean square roughness
σ_{rms}	Root mean square roughness
σ_{small}	Small-scale root mean square roughness
σ_{stat}	Static value of the electric conductivity
T	Absolute temperature
T	Transmittance
TCO	Transparent Conductive Oxide
TEM	Transmission Electron Microscopy
THz	Terahertz
t	Field transmission coefficient
t	Time
t	Groove depth (Sect. 9.2)
t_{coh}	Coherence time
τ	Time constant, relaxation time, lifetime
θ	Step function
ϑ	Temperature in °C
UV	Ultraviolet spectral region
V	Volume

VASE	Variable Angle Spectroscopic Ellipsometry
ν	Vibrational quantum number
VIS	Visible spectral region
VP	Cauchy's principal value of the integral
VUV	Vacuum ultraviolet spectral range
$W(l)$	Equilibrium population of l -th quantum level
ω	Angular frequency
ω_0	Angular eigenfrequency, resonance angular frequency
ω_{electr}	Resonance angular frequency of a purely electronic optical transition in a molecule
ω_p	Plasma (angular) frequency
ω_{vibr}	Resonance angular frequency of a purely vibronic transition in a molecule
$\tilde{\omega}_0$	Shifted with respect to local field effects resonance frequency
ω_{mm}	Transition frequency, resonance frequency in quantum mechanics
$\Delta\omega$	Spectral bandwidth
x	Position
XRR	X-ray reflection
Z	Statistical sum

Chapter 1

Introduction

Abstract In contrast to traditional solid state physics, the physical properties of thin solid films are to a large extent defined by the properties of their surfaces and internal interfaces. Despite of material properties, geometrical parameters like film thickness are therefore essential for adequate description of their properties. For accurate and reproducible adjustment of material and geometrical film properties, numerous film deposition and growth monitoring techniques have been developed and optimized.

1.1 General Remarks

50 Jahre bewusster Grübeleien haben mich der Frage: ‘Was sind Photonen?’ nicht näher gebracht. Heute glaubt zwar jeder Lump, er wüsste es. Aber sie täuschen sich

(engl: A total of fifty years of conscious brooding did not get me any nearer to answering the question: what are light quanta? Of course today every rascal believes he knows the answer, but he is wrong)

Albert Einstein, Letter to N. Besso, December 12, 1951 [1, 2]

... Denn eben wo Begriffe fehlen, da stellt ein Wort zur rechten Zeit sich ein ...

(engl. ...For at the point where concepts fail, at the right time a word is thrust in there...)

**Mephistopheles, in ‘Faust. Der Tragödie erster Teil’ (engl: Faust: The First Part of the Tragedy),
Johann Wolfgang von Goethe, 1808**

Today’s optical instrumentation becomes more and more complex. In order to guarantee durability and high optical performance of any optical component, its surfaces have to be over-coated with specially designed thin film stacks to achieve tailored optical properties as well as surface protection. Clearly, any improved or new optical technology may require modified or new optical coating designs, so that optical thin film design is of utmost importance for the whole field of applied optics. And it is an irony of history, that optical coatings have manipulated the behaviour of incident photon assemblies at surfaces quite reliably for decades,

although the above citation makes it clear that it is quite nontrivial to understand what is really incident to the surface whenever the light source has been switched on.

Traditionally, the optical properties of thin solid films form an interdisciplinary research and development field that combines facets of classical optics, classical electrodynamics, solid state physics and quantum mechanics into a specific branch of applied optics. In addition to that, in the last years, certain aspects of photonics, plasmonics and nano-optics have infiltrated traditional thin film optics, thus forming new sub-branches like nanostructured dielectric or metallic (plasmonic) optical films. All this makes the field of thin film optics more versatile and powerful—and of course more interesting. On the other hand, while gaining complexity, the optical coating research field appears less clearly arranged and structured. Thus, it may appear troublesome particularly for a beginner in this field to find an orientation in a somewhat confusing and quickly changing scientific environment. The present text shall provide assistance in this regard.

In order to avoid misunderstandings: For a (becoming) optical coating expert, it is absolutely necessary to start his scientific development studying textbooks on traditional thin film optics. Particularly when focusing on interference coating literature, one will find excellent monographs highlighting all aspects of classical optical coating design, such as for example the textbooks written by Macleod [3] and Thelen [4]. The practitioner thus becomes familiar with plenty of skills for constructing an optimal sequence of individual layers built from different materials with different individual layer thicknesses, which are to form a film stack that is to fulfill a required set of optical specifications (the *target performance*). Of course, it is implicitly assumed here that the optical constants of the layers are accurately known and mathematically described in a manner that makes them accessible to the favored design program (or algorithm). But in practice, optical material property aspects usually earn much less attention than the methods for optimizing layer thicknesses, i.e. geometrical construction parameters.

It is therefore the opinion of the author of the present book, that there is a misbalance between the amount of literature highlighting skills to optimize *geometrical coating parameters*, and books which focus on additional degrees of freedom in coating design that arise from the flexibility in optical coatings *material properties*. It is another main purpose of this book to contribute to a rebalancing of that situation. In addition, simple aspects of nanostructuring shall also be included in order to comply with modern development trends.

Nevertheless, we will start our excursion through optical coating science from *traditional* optical coatings. In Fig. 1.1, a multilayer stack is schematically presented that illustrates the possible construction of an optical coating. In this simple picture, the construction parameters are subdivided into purely *geometrical parameters* (written on right of the figure) and *material parameters* (written on left).

As it is illustrated in Fig. 1.2, geometrical and material parameters affect the optical properties of a coating (which may be defined through its characteristic matrix [5]) in a rather complicated manner, even when it is assumed to be optically

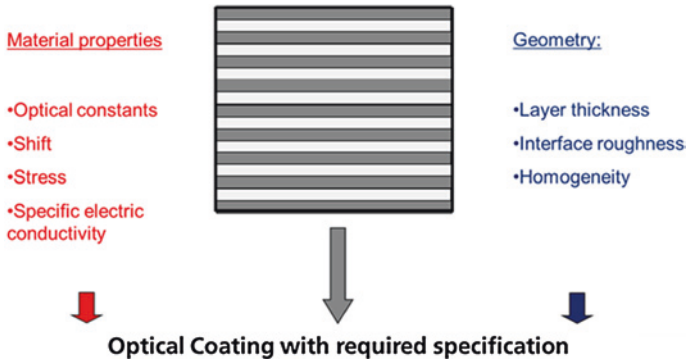


Fig. 1.1 Illustration of construction parameters which may define the performance of an optical coating

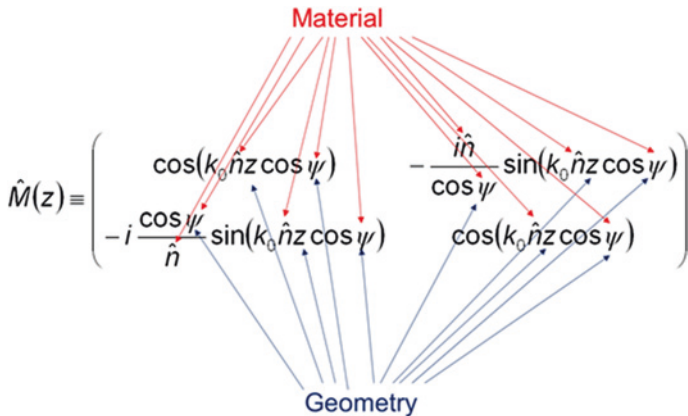


Fig. 1.2 Information on material and geometrical parameters in the characteristic matrix of a single film (here for p-polarisation)

homogeneous, optically isotropic, and with ideally smooth interfaces and surfaces. Thus, geometrical parameters affect the layer properties through the thickness (and principally through the incidence angle, which is a geometrical parameter of the measurement arrangement), while material parameters define the complex index of refraction as well as the propagation angle. By the way, the rather involved mathematical interconnection of material and geometrical coating parameters makes it so difficult separating these informations in practice when performing a re-engineering procedure. But for us it is sufficient to recognize, that both material and geometry aspects appear equally important in the mathematical description of optical coatings. Shortly spoken, this monograph stresses the material aspect of the whole problem.

Concerning linear optical material constants, in most sources they are given in terms of the real (n) and imaginary (k) parts of the *complex index of refraction* \hat{n} . Hereby, n is the so-called *refractive index* of a material, which gives access to the phase velocity of an electromagnetic wave travelling through the medium. The value k , which is the so-called *extinction coefficient*, describes the damping of the wave. Instead of k , sometimes the *absorption coefficient* α is used:

$$\alpha = 2\frac{\omega}{c}k = \frac{4\pi}{\lambda}k = 4\pi\nu k \quad (1.1)$$

Here ν is the so-called wavenumber, which is defined as the reciprocal value of the wavelength in vacuum λ . This absorption coefficient is identical to the damping constant fixed in Bouguer–Lambert–Beer’s law [6, p. 76], and its reciprocal value is called the *penetration depth* of electromagnetic irradiation into a medium.

1.2 Thin Film Physics and Solid State Physics

Formally, thin film physics might be regarded as an integral part of solid state physics, and many textbooks on solid state physics indeed contain some paragraphs dedicated to the specifics of thin films. Sometimes it is even believed that thin film physics form an applicative chapter to solid state physics. To the opinion of the author of this book, this is by far not the point. The basic models of thin film optics and solid state optics are quite different: In basic solid state optics, a three dimensional atomic arrangement is considered which ideally extends to infinity so that a surface or interface rather appears as a giant defect to the otherwise ideal solid. In thin film optics, infinite spatial extension is assumed only in two directions (which define what we call the *film plane*), while in the third dimension (which defines the *film axis*), the spatial extension of the system (the *film thickness*) is small enough so that it appears much lower than the coherence length of the light. Thus, surfaces and interfaces play an entirely different role in the basic solid state and thin film models.

Of course, no real solid extends to infinity, so that in real life we always have to deal with surface and interface contributions to the overall behaviour of a system. Hence, in practice, we always have a certain amount of atoms which are located in interface regions and therefore behave in another fashion than those located in the bulk of the material. It is the difference in the ratios between surface and bulk atoms which give rise to some specifics observed in the physical behaviour of thin films (Fig. 1.3).

Let us illustrate this statement with a few simple examples. It is rather astonishing, that specific morphologic features of real optical coatings have their macroscopic counterparts in nature. Thus, coatings prepared by evaporation techniques tend to show a *columnar microstructure*. For the sake of illustration, in Fig. 1.4 several columnar structures as obtained from SEM of evaporated coatings are opposed to photographs of essentially *macroscopic* columnar structures which are, in

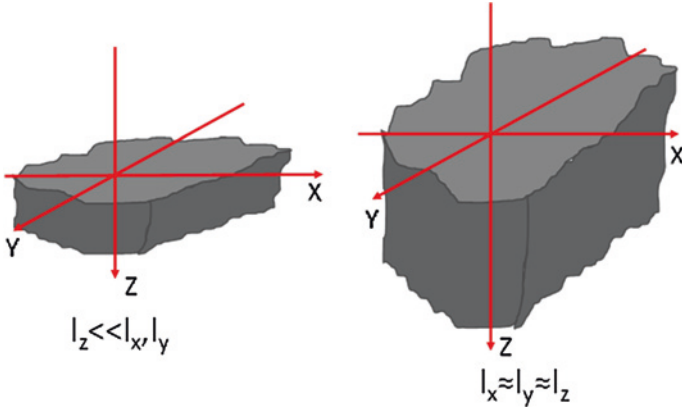


Fig. 1.3 Thin film (*left*) and bulk solid (*right*). On left, the x and y -axes define the film plane, while the z -axis defines the film axis

terrestrial conditions, usually formed as a result of volcanism. So, in Fig. 1.4 (right on top), we see the fracture edge of an approximately 300 nm thick magnesium fluoride layer. It has an astonishing similarity in appearance to a basaltic column assembly found on Iceland, except the difference in their sizes (Fig 1.4 left on top; the basaltic columns have a length of a few meters). Even more impressive is the rock cliff in Svalbard (Fig. 1.4, second row on left), which is composed from huge free-standing basaltic columns, with a height of the full assembly accounting for more than 100 m. Its thin film microscopic counterpart is presented in Fig. 1.4 in the second row on right; it shows free-standing columns at the fracture edge of an evaporated aluminum oxide film, deposited by EBE without heating, while the growth rate was 0.5 nm/s (courtesy of Hanno Heiße [7]). In this example, the solid material forms spatially isolated structures embedded in free space.

In the third row in Fig. 1.4, we see the opposite situation: The solid fraction forms some kind of matrix, while isolated pores appear as an inclusion in that solid host. And finally, in the fourth row (on bottom in the figure); we have a multilayer system shown on right together with a nice example of a macroscopic counterpart, namely a rock formation in the Sexten Dolomites.

Despite of their seeming geometrical similarity, the physical properties of sub-micro- and nano-columns and pores are quite different from those of their spectacular macroscopic counterparts. In order to get an impression the physical differences, let us compare the surface-to-volume ratio of a microscopic and a macroscopic rod. For the microscopic column, let us assume cylindrical geometry with a diameter $D = 50$ nm and a height $h = 200$ nm. For the macroscopic one, let the diameter be 5 m, and the height 20 m. From the equations for the Volume V and the surface area A of a cylinder, we have:

$$V = \pi \frac{D^2}{4} h; \quad S = \pi \frac{D^2}{2} + \pi D h \Rightarrow \frac{S}{V} = \frac{2}{h} + \frac{4}{D} \quad (1.2)$$

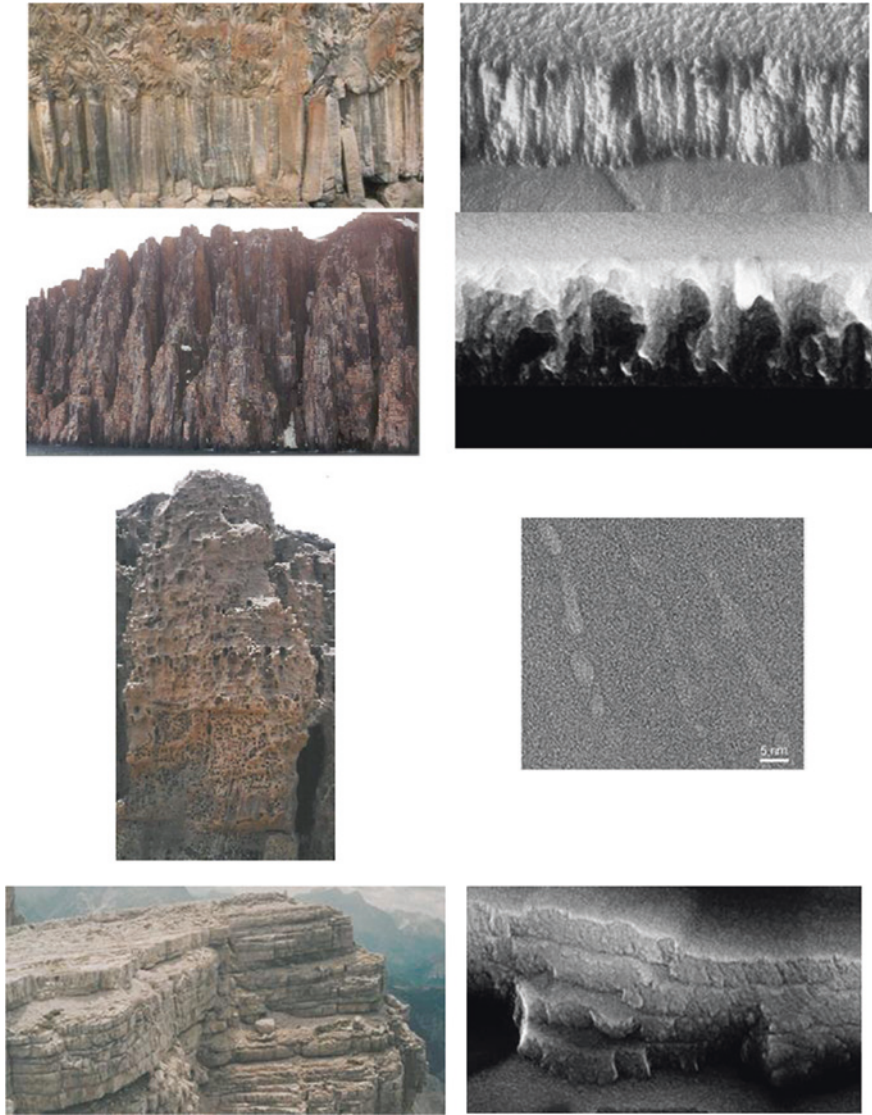


Fig. 1.4 Comparison between certainly macroscopic geologic formations (*on left*) and thin film structures (*on right*): *on top* basaltic columns at Aldeyjarfoss, Iceland an SEM image of the fracture edge of a magnesium fluoride layer [33]. *Second row* rock cliff (appr. 100 m high) at Alkefjellet, Svalbard, with huge free standing columnar structures and SEM image of the fracture edge of a strongly porous aluminum oxide layer with a thickness of appr. 200 nm. *Third row* Rather spheric pores in volcanic stones, Calheta, Porto Santo and closed pores in a niobium pentoxide coating (see later Fig. 7.5); *Bottom* Plane rock formation at Hochebenkofel, Sextner Dolomites, Italy; *Right on bottom* fracture edge of a multilayer coating, visualised by SEM [7]

Table 1.1 Typical spatial parameters of microscopic and macroscopic columnar structures

Geometrical parameter	(Sub-)Microscopic rod (coating)	Macroscopic rod (cliff)
D	50 nm	5 m
h	200 nm	20 m
S	353,00 nm ²	353 m ²
V	393,000 nm ³	393 m ³
S/V	$\approx 1/10 \text{ nm} = 10^8/\text{m}$	$\approx 1/\text{m}$

The result of this calculation is presented in Table 1.1.

Compared to the macroscopic columns, the significance of surface effects relative to volume effects is 10^8 times higher in the case of (sub-) microscopic columns. For nanorods or nanopores, the difference will even be larger. Therefore, in thin films, and generally in submicro- or nanostructured materials, surface effects are much more dominant than we would expect it from our daily experience, which essentially stems from rather macroscopic bulk systems. These surface contributions define the physical differences between thin films and macroscopic solids.

In daily life, we speak on the thin film when its spatial extension along the film axis (the film thickness) is small compared to a pre-selected spatial parameter. Thus, the “definition” of a thin film is ambiguous: A coating which is classified as a thin film with respect to mechanical protection purposes may be much thicker than an EUV interference coating. At the same time it may be much thinner than an interference coating designed for the THz spectral region. So that there exists no absolute definition what a thin film is. But with respect to its practical application, the quasi two-dimensionality of a thin film always offers the prospective possibility to replace volume functionality by surface functionality—a rather sustainable approach in a world with restricted resources.

1.3 A Few Words on Optical Coating Preparation

1.3.1 PVD and CVD Techniques

This book will definitely not provide an overview on thin film deposition techniques. Interested readers are referred to corresponding reviews, for example [8]. There are plenty of *Chemical Vapor Deposition* (CVD) and *Physical Vapor Deposition* (PVD) techniques, and their description could fill a single book alone.

In short, PVD techniques offer major methods for high quality optical coatings manufacture today. With respect to the fundamental transfer processes of the coating material into the vapour phase, they are subdivided into two main groups: evaporation and sputter techniques [8]. Sometimes, the ion plating techniques, which principally belong to evaporation techniques, are listed as a separate group of PVD techniques. Moreover, all these techniques may be distinguished

into their reactive and non-reactive versions. With respect to the major subject of this book—namely material properties—it is worth noting that highest refractive indices of oxide coatings are usually achieved by ion plating techniques. As a side effect, those coatings often suffer from a high compressive stress [9].

In every PVD process, the layer-forming atoms are generated through thermal or mechanical energetic impact on the surface of a starting material (evaporation material or *target* for sputtering techniques), and transported to the substrate by rather ballistic processes in vacuum conditions. On the contrary, in a CVD process, the constituents of a vapour phase react in heterogeneous reaction sequences to form the required solid film on the substrate surface. And, in contrast to PVD, CVD may principally be performed at atmospheric pressure. In optics, CVD deposition processes are not as widely distributed today as PVD techniques are. Major advantages of PVD processes are:

- Broad classes of accessible coating and substrate materials
- Simple control of the layer micro- and nanostructure by means of technically accessible (external) control parameters of the deposition process
- Widely distributed common know-how on technological parameter fields for producing high quality optical coatings with good adhesion and resistance to mechanical/environmental impact.

On the other hand, major disadvantages of PVD processes concern:

- Comparably low deposition rates and layer thicknesses
- Vacuum equipment is necessary
- Coating of components with complicated geometry appears troublesome.

Particularly with respect to the last mentioned disadvantage, CVD methods offer an alternative to PVD methods. While having been originally developed for coating inner surfaces of tubes, a primary advantage of their application is in the possibility of three-dimensional overcoating of surfaces of any shape.

It is worth mentioning another prospective optical coating deposition technique. *Atomic Layer Deposition* (ALD, earlier sometimes *Atomic Layer Epitaxy* ALE) is similar to CVD, although marking differences occur [10, 11]. Thus, in contrast to conventional CVD, the reactants are introduced into the reaction chamber successively, and the reaction is surface controlled with the film growing for a (sub) monolayer thickness per cycle only. Nevertheless, because of the close affinity of ALD to CVD, it is self-explanatory that the major potential of ALD processes in the optical coating branch is expected in situations when surfaces of complicated shapes are to be coated. Also, ALD has received increasing interest as coating technology, because it offers tight control of the film thickness [12]. Moreover, major oxide, fluoride, carbide, and nitride coating materials are accessible to ALD today [13]. The ALD process therefore seems most prospective when requirements of uniform coating of complicated by shape optical surfaces coincide with requirements of precise thickness control. So the major potential of ALD processes for optics is the coating of surfaces of complicated shapes; including strongly curved substrates as well as nanostructured (patterned) optical surfaces.

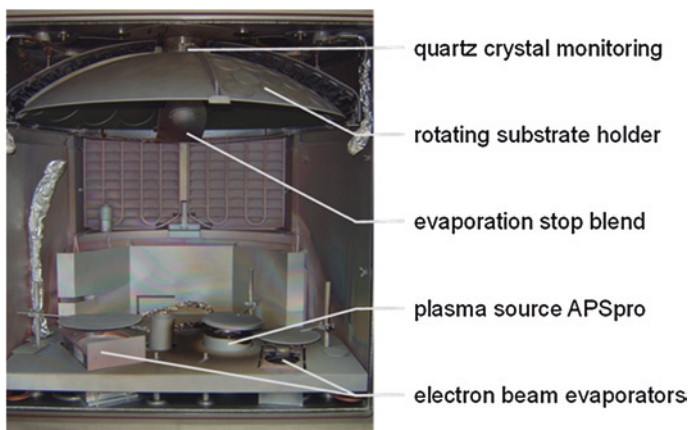


Fig. 1.5 Deposition system Leybold optics Syrus pro 1100

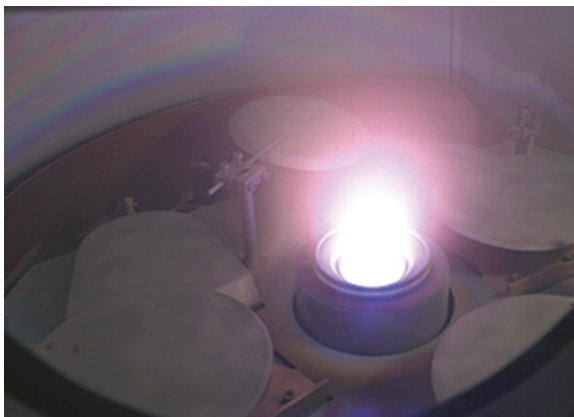
In this subsection, we will nevertheless concentrate on a selected and widely used PVD technique, namely the so-called *Plasma Ion Assisted Deposition* (PIAD) technique. The reason is that most of the experimental data shown in this book to illustrate the relevance of any theoretical considerations stem from samples deposited by PIAD.

1.3.2 Some Considerations on PIAD

Essentially, PIAD is accomplished as a typical (and in many cases reactive) electron beam evaporation technique, while the growing film is additionally bombarded with highly energetic particles from a plasma beam. The latter is generated by a Plasma Source such as the Leybold *Advanced Plasma Source* (APS). The APS itself has been introduced into practice in the 90th [14], and has got wide distribution in coating manufacture due to its outstanding performance. Thereby, noble (and in many cases also reactive) gas ions generated in the plasma source are accelerated by a Bias voltage (BIAS) which gives a rough estimate of the kinetic energy of the ions responsible for the assistance of the film growth [15]. Additionally, fast neutrals are generated by charge exchange and elastic collisions of beam ions with the background gas. Therefore, according to recently developed analytical models [16], high energetic ions as well as high energetic neutrals arrive at the substrate and modify the properties of the growing film.

Figure 1.5 gives an impression on the widely used deposition apparatus Leybold Optics Syrus pro 1100 equipped with two electron beam evaporators and an Advanced Plasma Source APSpro. Film growth can be controlled by quartz crystal monitors (compare [17]) as well as optical monitoring [17–19]. The deposition system shown in Fig. 1.5 is equipped with a broadband optical monitoring

Fig. 1.6 Advanced plasma source APS in action



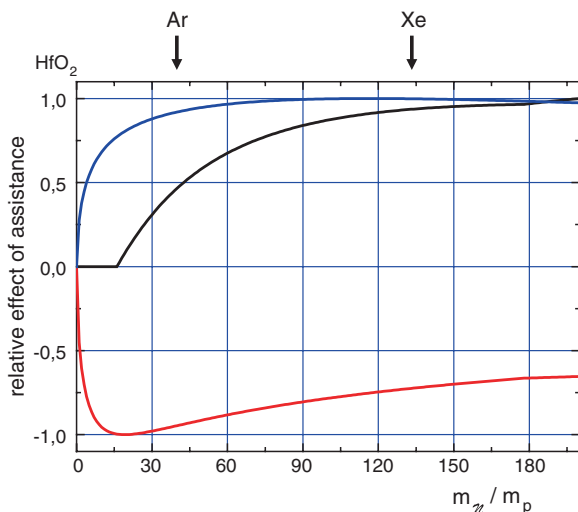
system OptiMon [20]; the light source is located in the semi-spherical cavity on bottom of the evaporation stop blend which is easily identified in Fig. 1.5. More details on this subject will be found in Chap. 5 of this book.

Just for getting an impression, Fig. 1.6 shows a photograph of the APS in action (in this case it is an argon plasma). The emission spectrum of the plasma can be used to control the plasma status and can even be combined with optical broadband monitoring of the film growth to accomplish all-optical in situ monitoring of PIAD processes [20].

While films deposited by conventional electron beam evaporation (EBE) are usually porous, the advantage of ion assisted (IAD) or plasma ion assisted deposition (PIAD) techniques is in their ability to produce dense coatings which appear less porous or even practically free of pores. According to diverse models, the underlying mechanism for the formation of denser films is the momentum transfer from the mentioned high energetic particles generated by the plasma source to the film forming species [21, 22]. It should therefore be possible to quantify the effect of assistance in terms of the film density, which can be measured for example by X-ray reflection XRR. We will demonstrate this at the example of hafnium dioxide films, because quite a lot of literature data is available on this interesting coating material.

Indeed, hafnium dioxide layers deposited by EBE without assistance at high substrate temperatures (around 300 °C) have been found to have a mass density in the region between 8.6–9.0 g cm⁻³. These data have been obtained when the oxygen flow during deposition was around 10–20 s ccm and the deposition rate 0.2 nm/s [23]. PIAD layers (substrate temperature 100 °C) deposited in otherwise similar conditions have higher densities between 9.1 and 9.4 g cm⁻³, when the assistance has been performed with argon as the noble gas (argon assistance). Even higher densities between 9.3 and 10.2 g cm⁻³ are reported when the assistance is performed with xenon instead of argon (xenon assistance) [24]. Plasma ion assistance therefore leads to a clearly measurable effect on the material properties of the manufactured coating.

Fig. 1.7 Simulated relative increase in mass density (blue line), noble gas atom incorporation (black) and stoichiometry deficit (red) for PIAD of hafnium dioxide. For details of the simulation see Appendix A



As it may be shown by rather simple simulations (see Appendix A), the observed increase in density is consistent with the assumption of momentum transfer processes resulting from bombardment of the growing film by highly energetic noble gas atoms or ions. Figure 1.7 shows the result of such a simulation for the case of PIAD of hafnium dioxide layers. The blue line illustrates the expected gain in mass density as a function of the (fictive) mass number of incident high energetic ions or atoms (term m_n in Appendix A). Arrows mark the special cases of Ar and Xe assistance. It is clearly to be seen, that the gain in mass density (or densification) is always larger than zero, while it is higher for xenon, in agreement with the experimental findings mentioned before. At the same time the assistance leads to a stoichiometry deficiency (or understoichiometry) (here a relative lack of oxygen—the red line in Fig. 1.7, term m_z in Appendix A), which can be compensated by adding a suitable amount of reactive gas (here oxygen) during deposition. And finally, according to the simulation, the assistance is expected to result in incorporation of the corresponding noble gas atoms into the film (term m_n in Appendix A). This effect may account up to several atomic percent of noble gas in the film [24]. In practice, the mentioned stoichiometry deficits and contamination levels appear to be at horrible levels when comparing for example with standards accepted in semiconductor technology. But nevertheless optical coatings work in practice, while accurate quantum mechanical modeling of their optical material properties appears to be a challenging task [25]. This is less caused by a lack of corresponding solid state models, but rather by the large uncertainties in the films local atomic structure as well as in the experimental input parameters obtained from measurements of practically produced samples.

In finishing these considerations it is worth looking on Fig. 1.8. It shows refractive indices (at a wavelength of 400 nm) of hafnium dioxide layers deposited by different deposition techniques. Note the enormous span in refractive indices

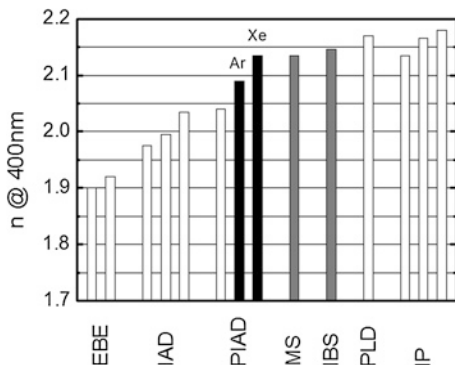


Fig. 1.8 Range of refractive indices reported for hafnium dioxide layers depending on the deposition technique. EBE data taken from reference [35]; IAD data taken from reference [36, 37]; PIAD data taken from references [24, 38]; MS and IBS data extrapolated from reference [39]; PLD data taken from reference [40]; IP data taken from references [37, 41, 42]

which can be realized in practice. Lowest indices are obviously achieved with EBE, and highest by means of sputtering, PLD, and IP. The mentioned PIAD technique usually delivers refractive indices in between the mentioned extremal cases. It is thus quite versatile and therefore suitable as the reference method in a book which is dedicated to optical coating material properties. Thus, with respect to the title of this book, we emphasize that it is the *span* in optical film constants such as shown for the particular case of hafnium dioxide layers in Fig. 1.8, which is in the focus of this monograph.

1.3.3 Property Correlations

For the design of real interference multilayer coatings (compare Fig. 1.1 and later Chap. 4), however, one needs at least *two* coating materials with a relevant refractive index contrast. This is necessary in order to generate sufficiently intense internal reflections of the light inside the multilayer, so that one can fit a predefined specification by a tricky interplay of constructive and destructive interference of multiply reflected light beams. So at least one high index and one low index material are required, both being transparent in the specified spectral region. Moreover, minimization of thermal shift (see Sect. 5.1.2) is of advantage as well as control of the mechanical stress. As experience shows, both thermal shift and mechanical stress are closely related to the kind and degree of porosity which defines the morphology of the coating (Chap. 7).

Empirically it appears that the porosity of practically deposited coatings can be controlled by choice of the deposition method and deposition parameters. Depending on size and shape of the pores, as well as ambient conditions, pores can

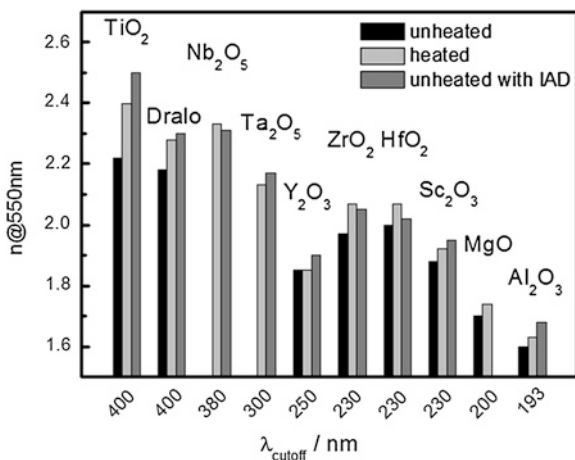


Fig. 1.9 Refractive indices of standard oxide films as prepared with different deposition conditions. Dralo™ denotes a commercial material mixture composed from titanium dioxide and aluminum oxide

by empty or filled with water, thus giving rise to what we call the shifting behavior. But in any case it is expected that a porous coating has a lower refractive index than its dense counterpart, because both air and water have lower refractive indices than most of the coating materials that we will discuss in this book. Therefore, at least for the high index oxide coatings, a first guess on the degree of porosity can be made comparing the refractive indices of differently prepared samples.

Basing on catalogue data [26], the refractive indices (here at 550 nm) of some selected relevant oxides as obtained from different deposition techniques are visualised in Fig. 1.9. The general trend is obvious: Films prepared on unheated substrates by evaporation without assistance have the lowest indices, so they are expected to exhibit highest porosity. Substrate heating leads to higher indices, hence it should be helpful to reduce porosity. Suchlike correlations are often illustrated in terms of the so-called structure zone models [27–31]. Corresponding to the data from Fig. 1.9, high indices (and low porosity as well as a weak or vanishing shift) are also expected for coatings prepared by means of IAD or PIAD.

Finally, Fig. 1.10 gives a nice example on how versatile optical “constants” may appear in practice. The figure shows examples on measured refractive indices of silicon dioxide and titanium dioxide layers at 550 nm, while the samples have been deposited by different techniques. All these data stem from different contributions to a single proceedings volume of a German OTTI workshop [32]. Variations in density, porosity, stoichiometry, atomic structure, contamination level and the like result in a rather large span of optical constants obtained. It appears obvious that the indication of a single refractive index for titanium dioxide layers (say, $n = 2.4$) does not make any sense in practice. In this book, we will therefore rather focus on the *correlation* between different material properties than on their absolute values.

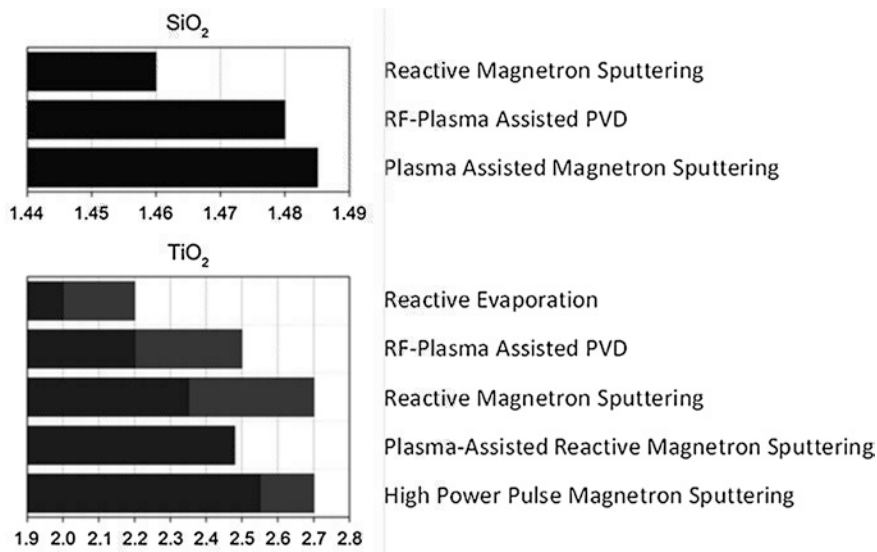


Fig. 1.10 Silicon dioxide and titanium dioxide refractive indices at 550 nm, as collected from reference [32]

1.4 To the Content and Organisation of this Book

The present monograph is subdivided into 4 main parts. The first part (Basics) is to give a concise overview on dispersion models, Fresnel's equations and basic optical properties of single and multilayer coatings. This part summarizes main equations necessary to perform a direct (forward) search procedure in thin film optics, i.e. calculate the thin film spectrum from given optical constants and construction parameters of a coating. This is standard material that can be found in many sources, so that it is rather summarized than explained, as already mentioned in the preface to this book. In contrast to [33, 34], in this book we will deal with linear optical properties of the films only.

The second part (reverse search problems) is written in a more explaining style. It deals with selected aspects of coating characterization and design tasks, i.e. the determination of optical constants and/or construction parameters from given spectral characteristics. Particular emphasis is given here to single film characterization, because before designing, the optical constants of the individual coating materials must be known. Taking corresponding data from external literature sources obtained from maybe other deposition techniques and conditions is not very helpful, as it should be clear from the previous subsection. This explains the inclusion of the rather extended characterization section into this book. The design section is comparably short; it rather deals with material and feasibility aspects of design problems than with the description of coating design techniques.

The third part of this book summarizes measured optical properties and experimentally established property correlations of selected pure coating materials. The fourth and last part is dedicated to examples of nanostructured coatings and surfaces as well as different kinds of material mixtures.

There are four appendices at the end of this book, which contain additional (and mostly theoretical) material on selected facets of the topic of this book. Reading these appendices is not really necessary for understanding this book, but—to the opinion of the author—quite useful.

It should be emphasized that a substantial part of the demonstrated experimental material—especially when stemming from PIAD experiments—has been generated at Fraunhofer IOF Jena, Germany. This is not always explicitly mentioned, instead, it is usually referred to the original publication where these results have been reported to the public for the first time. This remark also concerns the results of round robin experiments performed together with cooperating research institutes and companies. Here, only previously published experimental material has been included into this book while referring to the original publication. From the latter, the interested reader can obtain information about the participants of the experiments and further details on their particular contribution to the extent as the participants were willing to disclose them.

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