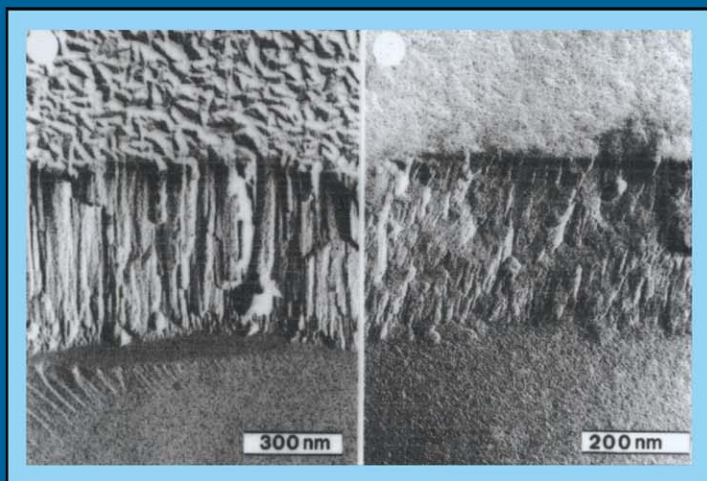


# *Coatings on Glass*

*Second, revised edition*

H.K. PULKER



ELSEVIER

# *Coatings on Glass*

Cover illustration:

AlN films

(left)

$E_{\text{kin}} = \text{low}$

$\rho = \text{low}$

$n_{550} = 1.98$

$\sigma_{\text{tens.}} = 0.3 \text{ GPa}$

(right)

$E_{\text{kin}} = \text{high}$

$\rho = \text{high}$

$n_{550} = 2.12$

$\sigma_{\text{comp.}} = -0.9 \text{ GPa}$

AlN polycrystalline

E. Rille, R. Zarwash and H.K. Pulker, Thin Solid Films 228 (1993) 215

Th. Müller and H.K. Pulker, Thin Solid Films 246 (1994) 42

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H.K. PULKER

*Basic Research Laboratory, Balzers AG, Liechtenstein*

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## DEDICATION

This monograph is dedicated to three distinguished personalities who have played a decisive role in the development and spread of the industrial manufacture of thin films produced under vacuum by physical methods:

Prof. Dr. Dr.h.c. Max Auwärter  
Founder and first President  
of the BALZERS AG

Dr. Albert Ross  
President of the BALZERS AG

Dr. Otto Winkler  
Director of the BALZERS AG

Hans. K. Pulker

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FOREWORD  
of the First Edition

The subject matter of this book *COATINGS ON GLASS* includes a wealth of information for physicists, chemists and engineers who need to know more about thin films for research purposes, or who want to use this special form of solid material to achieve a variety of application-oriented goals.

This particular publication is exceptional because the author makes available his extensive theoretical and practical experience which has been acquired over more than 20 years of intensive work on thin films. He has been concerned with all details that have an influence on the final product and can thus describe with great thoroughness the properties of all glass-type substrates, dealing also with very difficult questions concerning surface physics.

Glass can be produced by a variety of methods. The manufacturing process and the chemical composition determine how resistant a particular glass is to its environment. There are also different processes for finishing the surface of glass and this, together with the two aforementioned factors, determines the surface characteristics. Apart from inorganic glass also organic glass and plastic materials are considered.

Today there are two preferred groups of methods for the production of thin films: Chemical vapour deposition and physical vapour deposition under vacuum; the three major technologies of the latter being sputtering, evaporation, and ion plating. These are discussed in detail. The author's wide experience allows him to give many valuable tips in the discussion of how to produce a vacuum with a desired residual gas atmosphere using appropriate vacuum techniques. He has also studied mechanical and optical film properties as well as film thickness measurement methods, and this too is included in the book. Information on calculation methods which allow complex film systems to be developed is also given. Precise calculations and extremely accurate measurements are the basis for the production of thin films in computer controlled coating systems.

Applications of thin films are also given an important place in the book. The company in which the author works is world famous for its thin film products.

In summary, this work could be called a sort of formulary on the subject of glass and thin films written by a scientist for scientists and technical people. It goes beyond the subject matter indicated by the title, filling in the gap which has existed until now in the available technical literature.

M. Auwärter



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## PREFACE of the First Edition

Hans K. Pulker is an old friend for whom I have always had the highest regard. He is also a thin-film worker with a well-deserved international reputation for careful and original scientific work. I was delighted, therefore, when I heard that he was in the course of writing a book on coatings on glass. It is a source of great satisfaction and pleasure to me to write the preface so that I can be associated even in this minor way with what promises to be one of the standard works of reference in this important and ever-growing field.

All of us who work in the field of thin films have had more than our share of frustrating experiences with apparently inexplicable failures of a coating process. Frequently these involve well-developed techniques which have been running quietly and efficiently for some time. Suddenly coatings no longer adhere to the substrates although we are apparently following our standard procedure. Or stains appear in coatings on carefully prepared substrates. Sometimes absorption is high when it should be low, or cloudy scattering is apparent. Occasionally the problems are even more insidious, appearing only at a much later stage when components have already been supplied to a customer and are already in an optical system. I dwell on optical coatings because that is my own particular field but similar problems plague other areas of thin-film work. Apart from the weather, bad luck has often seemed the only reason for such troubles and even lucky charms have been seen in coating shops.

The past decade has seen considerable changes. We still suffer from unforeseen problems but gradually we are coming to understand the complex physics and chemistry governing the phenomena. We are used to dealing with thin films on a macroscopic scale and indeed it is their macroscopic properties in the main that we seek to produce with our coatings. These macroscopic properties, however, are entirely determined by film microstructure and it is only when we begin to understand the microstructure on an atomic scale and the physics and chemistry associated with it that we can appreciate the source of our problems and begin constructively to overcome them and to advance.

Films and substrates are held together by very short range forces, the bonds between one atom and the next. The mechanical properties of the films, including their intrinsic stress, are ultimately determined by these same bonds and their interaction with the microstructure. Their behaviour at surfaces can be greatly modified by minute quantities of impurity and they can be blocked completely by one molecular layer of contaminant. Adsorption is a particularly important process in thin films which must also be understood on an atomic scale.

Our understanding of film systems must begin with the nature of the surface on which they are deposited. Glass surfaces, the subject of this book, are particularly complex because of the nature of glass itself. Because of the gross effect of even

minute contamination, cleaning is extremely important. Significant sections of the book are devoted to these topics followed by surveys of the bewilderingly extensive array of processes for thin-film deposition, techniques for measurement and characterization, fundamental film properties and optical coatings.

Hans K. Pulker himself has made notable contributions to the improvement of our understanding of the physics and chemistry of thin films and to deposition processes. The subject is vast and the literature extensive but scattered through journals in many different disciplines. It is difficult to know where to begin a study of the subject. I should say that it *was* difficult because the situation has changed with the publication of this book.

H. A. Macleod

AUTHOR'S PREFACE  
of the First Edition

When the Elsevier Scientific Publishing Company first invited me to write a monograph on *COATINGS ON GLASS*, I was hesitant because of the enormous amount of work involved. However, after critically examining my own collection of literature on thin films and glass, and considering the amount of pertinent information available in the scientific libraries of both the Balzers AG and the Swiss Federal Institute of Technology in Zürich, I changed my mind.

Dr. A. Ross, President of the Balzers AG until the end of 1982, encouraged me with the project, and his successor Dr. G. Zinsmeister, continued this support. I was thus able to notify the publisher that I could accept their invitation.

Much of the material in the present work was originally prepared for lectures presented at the Institute of Physical Chemistry at the University of Innsbruck in Austria. However, to limit the length of the work some elementary material has been eliminated, leaving room for new information and details on technical processes so that the topic could be covered comprehensively. It was not my intention to publish in-depth studies of any particular area but rather to provide a well founded background from which individual interests in various directions could be developed by the specialist or the newcomer to the field.

Following a history of glass and films presented as an introduction in Chapter 1, the Chapters 2 to 4 of this monograph attempt to outline the present-day knowledge of glass, with particular attention given to such factors as structure and composition and how they influence the properties of the material. The condition of the substrate surface is of primary importance in the coating process and therefore the generation, cleaning and properties of the glass surface is treated extensively. In addition to inorganic glass, organic glass and plastics are also discussed.

There has been a close interrelation between glass and thin films for a long time. Thin films on glass are used both for scientific and industrial purposes. One of the most important requirements placed on industrial coatings is that they adhere well to the substrate surface, particularly if they are to be subjected to extreme environmental conditions. This topic is treated in Chapter 5.

There are many chemical and physical methods for producing thin films with reproducible characteristics on a variety of substrates. A distinction is also made between wet and dry film formation methods. In some of these methods the depositions are carried out in air at normal atmospheric pressure or in the presence of protective gases and still others are carried out under vacuum. However, not all these methods are suitable for coating glass substrates because of their insulating nature and the relatively low thermal stability of many inorganic and practically all organic glasses. In Chapter 6 suitable coating methods and the plants for them are described. The various methods for the determination of film thickness and deposition rate are treated in Chapter 7.

Thin films generally have large surface to volume ratios, and consequently the extended surface usually has a large influence on the film properties. Structure, microstructure, chemical composition, mechanical and optical properties, etc. of films deposited by different methods are described and discussed in Chapter 8.

Finally, in Chapter 9, relevant industrial and scientific applications for thin films on glass are given.

The bibliography for this monograph does not pretend to be more than a selected one. The references cited are mainly original investigations, but review articles and books containing supplementary references are also listed.

Acknowledgements are made to Prof. Dr. M. Auwärter and Dr. A. Ross (Balzers AG) as well as to Dr. H. Dislich (Schott Glaswerke) for valuable discussions and advice.

Further thanks are given to the scientists and technologists of various other industrial companies and scientific institutes who gave their support to the author, making available many figures and valuable information. Here particularly must be mentioned: Dr. Ian Seddon (Optical Coating Labs. Inc., Santa Rosa, CA, USA), Dr. G. Kienel and Ing. G. Deppisch (Leybold Heraeus GmbH, Köln, FRG), Dr. K. Deutscher (Leitz, Wetzlar, FRG), Dr. H. Bach (Schott, Mainz, FRG), Dr. F. Geotti-Bianchini (Stazione Sperimentale del Vetro, Murano-Venezia, Italy), Dr. C. Misiano (Selenia SpA, Roma, Italy), Prof. Dr. R. W. Hoffman (Case Western Reserve University, Cleveland, OH, USA), Prof. Dr. R.Th. Kersten (Technische Universität, Berlin), Prof. Dr. H. A. Macleod (Optical Sciences Center, University of Arizona, Tucson, AR, USA) and Dr. E. Pelletier (Ecole Nationale Supérieure de Physique, Marseille, France).

The author is also very much obliged to friends and colleagues for their engaged assistance during the preparation of this book. Special thanks are due to Dr. O. Winkler, Dr. E. Ritter, Dr. G. Trabesinger and Prof. H.A. Macleod for critical reading of the manuscript and for their stimulating comments, and to Mr. W. Frischknecht (Fri-Grafik, Vaduz, Liechtenstein) for drawing most of the figures and to Mr. and Mrs. L. Hilty (printing office, Schaan, Liechtenstein) for preparing the camera-ready manuscript.

Last not least it is a pleasure to acknowledge the assistance of the staff of Elsevier Science Publishers in Amsterdam and to thank Mrs. A. Ruhe-Lodge, Miss K. O'Day and Dr. A.J. Perry for language corrections.

Hans. K. Pulker

## AUTHOR'S PREFACE

The importance of inorganic and organic glass in numerous technical and scientific applications is rapidly growing. Glass in its broadest sense is an important substrate for thin film coatings. Chemistry and physics occupy a central position in the treatment of both materials. It is therefore assumed that the reader – students, engineers, scientists – already has suitable knowledge in this field.

Coatings on glass and polymers are found today in an increasing number ranging from the architectural and automotive sector, the diverse applications in technical and scientific optics to various sophisticated high-tech structures. Coatings are used in practically all optical and electro-optical devices. They are frequently the ultimate determinants of performance.

The first edition of this book started in 1984 and had four unchanged impressions 1984, 1985, 1987 and 1996. It was translated into Chinese and printed in China 1987. Now its content is revised and updated. The emphasis was and still is pragmatic providing closer insight into the coating business and the properties of glass and thin films, particularly for optical purposes.

There are many people that have given me their support and advice, and the names of the people noted here have played a major role in the success of this edition.

I would like to acknowledge the support given to me by the management of the Balzers and Leybold Group during preparation of the manuscript, in particular, Mr. Andreas Vogt. I also thank Dr. Elmar Ritter and Dr. Günter Bräuer, also at Balzers and Leybold, and Dr. Angela Duparré at the Fraunhofer Institute in Jena, Germany for their unflagging encouragement during the writing of the manuscript.

My friend, Dr. Carlo Misiano, President of the Centro Tecnologie del Vuoto in Carsoli, Italy as well as my colleagues at the University of Innsbruck, Austria were also very generous with their time and, through many stimulating conversations, helped me work through numerous questions that came up during the writing.

Special thanks are due to Mrs. Iris M. Kündig-Hänni, who gave me critical support in the technical preparation of the manuscript. Dr. Nanning van der Hoop, Publication Manager for Physics and Astronomy at Elsevier Science BV in Amsterdam, The Netherlands, deserves sincere thanks for his suggestion to actually undertake the update of this book.

Finally, my deepest thanks to my wife, Marianne, who has supported me with patience, quiet encouragement and understanding during the writing.

Hans K. Pulker

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## TABLE OF CONTENTS

	DEDICATION.....	v
	FOREWORD.....	vii
	PREFACE.....	ix
	AUTHOR'S PREFACE I.....	xi
	AUTHOR'S PREFACE II.....	xii
Chapter 1	INTRODUCTION AND HISTORY.....	1
	References.....	5
Chapter 2	COMPOSITION, STRUCTURE AND PROPERTIES OF INORGANIC AND ORGANIC GLASSES.....	7
2.1	Glass-Forming Inorganic Materials.....	7
2.1.1	Crystallite Theory.....	8
2.1.2	Random Network Theory.....	9
2.1.3	Phase Separation, Devitrification.....	10
2.1.4	Glass Forming Organic Materials.....	11
2.1.5	Crystalline and Amorphous Behaviour of Polymers.....	12
2.2	Thermal Behaviour of Inorganic and Organic Glasses.....	12
2.3	Mechanical Properties of Inorganic Glasses.....	14
2.4	Chemical Properties of Inorganic Glasses.....	15
2.5	Electrical Properties.....	17
2.6	Optical Properties.....	19
2.7	Materials Transparent in Ultraviolet and Infrared.....	21
2.8	Photochromic Glasses.....	24
2.9	Glass Ceramics.....	27
2.10	Glass Materials for Advanced Technology and for Selected High Precision Applications.....	31
2.10.1	Laser Glasses.....	32
2.10.2	Glass Ceramics and Ultra Low Expansion Glass Optics...	32
2.10.2.1	Laser Gyroscopes.....	33
2.10.2.2	Space Telescopes.....	33
2.10.2.3	Large Ground-Based Optical Telescopes.....	34
2.10.3	Glasses for Photonics.....	34
2.10.4	Glasses for the Building Industry.....	35
2.10.4.1	Thermal Insulation.....	35
2.10.4.2	Noise Reduction.....	35
2.10.4.3	Safety Improvement.....	36
2.10.4.4	Fire Prevention.....	36



2.10.4.5	Solar Protection.....	36
	References.....	36
Chapter 3	NATURE OF A SURFACE.....	40
3.1	Characterization of a Surface.....	40
3.1.1	Structure of a Surface.....	41
3.1.2	Chemical Composition of a Surface.....	42
3.1.3	Energy of a Surface.....	44
3.1.4	Morphology of a Surface.....	45
3.1.5	Interactions Solid/Gas and Solid/Solid.....	47
3.2	Production of Glass Surfaces.....	50
3.2.1	Drawing and Casting.....	50
3.2.2	Pressing and Moulding.....	51
3.2.3	Grinding and Polishing.....	52
	References.....	57
Chapter 4	CLEANING OF SUBSTRATE SURFACES.....	60
4.1	Cleaning Procedures.....	61
4.1.1	Cleaning with Solvents.....	61
4.1.1.1	Rubbing and Immersion Cleaning.....	62
4.1.1.2	Vapour Degreasing.....	63
4.1.1.3	Ultrasonic Cleaning.....	63
4.1.1.4	Spray Cleaning.....	64
4.1.2	Cleaning by Heating and Irradiation.....	64
4.1.3	Cleaning by Stripping Lacquer Coatings.....	65
4.1.4	Cleaning in an Electrical Discharge.....	66
4.1.5	Cleaning Cycles.....	67
4.1.6	Cleaning of Organic Glass.....	68
4.2	Methods for Control of Surface Cleanliness.....	69
4.3	Maintenance of Clean Surfaces.....	70
	References.....	71
Chapter 5	GLASS AND THIN FILMS.....	73
5.1	Correlation between Glass and Thin Films.....	73
5.2	Adhesion between Substrate and Film.....	75
5.2.1	Methods of Adhesion Measurement.....	77
5.2.1.1	Mechanical Methods.....	78
5.2.1.2	Non-Mechanical Methods.....	80

5.2.2	Causes of Adhesion.....	83
5.2.2.1	Interface Layers.....	83
5.2.2.2	Types of Bonding.....	84
5.2.3	Parameter Influencing Adhesion.....	86
5.2.3.1	Coating and Substrate Materials.....	87
5.2.3.2	Substrate Preparation.....	87
5.2.3.3	Influence of the Coating Method.....	88
5.2.3.4	Aging.....	88
5.2.4	Practical Aspects of Adhesion Measurement.....	88
5.2.4.1	Scotch Tape Test.....	89
5.2.4.2	Direct Pull-Off Method.....	90
5.2.4.3	Scratch Method.....	92
5.2.5	Final Comments to Adhesion.....	98
	References.....	98
Chapter 6	FILM FORMATION METHODS.....	103
6.1.	Subtractive Methods.....	103
6.1.1	Chemical Processes.....	103
6.1.1.1	Surface Leaching.....	103
6.1.2	Physical Processes.....	104
6.1.2.1	High Energy Particle Bombardment.....	104
6.2	Additive Methods.....	105
6.2.1	Chemical Film Formation Processes.....	105
6.2.1.1	Deposition of Metal Films from Solutions.....	105
6.2.1.2	Deposition of Oxide Films from Solutions.....	107
6.2.1.2.1	Immersion or Dip-Coating.....	107
6.2.1.2.1.1	Formation, Structure, Optical and Mechanical Properties.....	107
6.2.1.2.1.2	Coating Procedure.....	121
6.2.1.2.1.3	Trends in Sol-Gel Development and Processing.....	126
6.2.1.2.2	Spin Coating.....	127
6.2.1.3	Deposition of Organic Films from Solutions.....	128
6.2.1.4	Chemical Vapour Deposition at Low Temperatures.....	130
6.2.1.4.1	Atmospheric-Pressure and Low-Pressure CVD.....	134
6.2.1.4.1.1	Spray Coating.....	134
6.2.1.4.1.2	Atmospheric-Pressure CVD.....	139
6.2.1.4.1.2.1	Compound Films.....	141
6.2.1.4.1.2.2	Metal Films.....	144
6.2.1.4.1.3	Low-Pressure CVD.....	149
6.2.1.4.2	Plasma-Activated and Photon-Activated CVD.....	150
6.2.1.4.2.1	Plasma-Activated CVD.....	150
6.2.1.4.2.2	Photon-Activated CVD.....	155
6.2.1.5	Physical Vapour Deposition.....	156

6.2.1.5.1	Vacuum Technology.....	157
6.2.1.5.1.1	Vacuum Pumps.....	161
6.2.1.5.1.1.1	Mechanical Displacement Pumps.....	161
6.2.1.5.1.1.2	Diffusion Pumps.....	165
6.2.1.5.1.1.3	Molecular Pumps.....	168
6.2.1.5.1.1.4	Cryo Pumps.....	172
6.2.1.5.1.2	High-Vacuum Process Systems.....	174
6.2.1.5.2	Film Deposition by Evaporation and Condensation in High Vacuum.....	185
6.2.1.5.2.1	Evaporation.....	186
6.2.1.5.2.2	Energy, Velocity and Directional Distribution of the Vapour Atoms and Thickness Uniformity of the Films....	190
6.2.1.5.2.3	Efficiency of Energy and Mass.....	205
6.2.1.5.2.4	Evaporation Techniques.....	207
6.2.1.5.2.5	Transit of the Vapourized Species Through the Reduced Atmosphere.....	214
6.2.1.5.2.6	Condensation and Film Formation.....	215
6.2.1.5.2.7	Evaporation Materials.....	219
6.2.1.5.2.8	Evaporation Plants.....	223
6.2.1.5.3	Film Deposition by Cathode Sputtering.....	230
6.2.1.5.3.1	General Considerations.....	230
6.2.1.5.3.2	Sputtering Threshold and Sputtering Yield.....	235
6.2.1.5.3.3	Ejection of other Particles and Emission of Radiation.....	239
6.2.1.5.3.4	Ion Implantation.....	240
6.2.1.5.3.5	Alterations in Surface Films, Diffusion and Dissociation.	241
6.2.1.5.3.6	Sputtering Rate.....	241
6.2.1.5.3.7	Particle Velocity and Energy.....	243
6.2.1.5.3.8	Angular Distribution.....	243
6.2.1.5.3.9	Composition of the Sputtered Material.....	244
6.2.1.5.3.10	The Gas Discharge.....	244
6.2.1.5.3.11	State of the Art in Industrial Magnetron Sputtering.....	256
6.2.1.5.3.12	Ion Beam Sputtering.....	258
6.2.1.5.3.13	Thickness Uniformity and Mass Efficiency in Sputtering	259
6.2.1.5.3.14	Sputtering Materials.....	262
6.2.1.5.3.15	Sputtering Plants.....	265
6.2.1.5.3.16	Comparison Evaporation and Sputtering.....	265
6.2.1.5.4	Film Deposition by Ion Plating.....	267
6.2.1.5.4.1	Characteristics of Ion Plating.....	268
6.2.1.5.4.2	Advantages of Ion Plating.....	274
6.2.1.5.4.3	Applications of Ion Plating.....	277
6.2.1.5.5	Reactive Deposition Processes.....	280
6.2.1.5.5.1	General Considerations.....	280
6.2.1.5.5.2	Reactive Evaporation.....	281
6.2.1.5.5.3	Activated Reactive Evaporation.....	286

6.2.1.5.5.4	Reactive Sputtering.....	290
6.2.1.5.5.5	Reactive Ion Plating.....	293
6.2.1.5.6	Plasma Polymerization.....	294
	References.....	300
Chapter 7	FILM THICKNESS.....	318
7.1	General Considerations.....	318
7.2	Methods Applicable to all Types of Films.....	319
7.2.1	Interference Methods.....	319
7.2.2	Stylus Methods.....	323
7.3	Methods Applicable to PVD Films.....	324
7.3.1	Optical Reflectance and Transmittance Measurements.....	324
7.3.2	Oscillating Quartz-Crystal Microbalance.....	328
7.3.3	Vapour-Density Measurement by Mass Spectrometry.....	335
7.4	Trends in Monitoring Technology.....	337
	References.....	339
Chapter 8	PROPERTIES OF THIN FILMS.....	343
8.1	Structure.....	343
8.2	Microstructure.....	354
8.3	Chemical Composition.....	364
8.3.1	Surface Analysis.....	364
8.3.2	Depth Profiling.....	367
8.4	Mechanical Properties.....	373
8.4.1	Stress.....	374
8.4.2	Hardness and Abrasion.....	385
8.4.3	Density.....	389
8.5	Chemical and Environmental Stability.....	390
8.6	Optical Properties of Thin Films.....	394
8.7	Relation between Density, Stress and Optical Film Properties.....	413
8.8	Electro-Optical Materials and their Properties.....	414
	References.....	417
Chapter 9	APPLICATION OF COATINGS ON GLASS.....	429
9.1	General Considerations.....	429
9.2	Calculation of Optical Film Systems.....	433
9.3	Antireflective Coatings.....	437

9.3.1	Single-Layer Antireflection Coatings.....	437
9.3.2	Double-Layer Antireflection Coatings.....	440
9.3.3	Multilayer Antireflection Coatings.....	441
9.3.4	Antireflection Coatings at Oblique Incidence.....	444
9.3.5	Inhomogeneous Antireflection Coatings.....	444
9.3.6	Applications of Antireflection Coatings.....	445
9.4	Rear Surface Mirrors, Surface Mirrors and Beam Splitter Mirrors.....	446
9.4.1	Rear Surface ACE Mirrors.....	447
9.4.2	Metal Film Surface Mirrors.....	447
9.4.3	Beam Splitter Mirrors.....	452
9.4.4	Neutral Density Filters.....	458
9.4.5	Dielectric Mirrors.....	458
9.4.6	Cold Light Mirrors and Heat Mirrors.....	460
9.4.7	Laser Coatings.....	463
9.4.8	Artificial Jewels.....	466
9.5	Separation of Light by Filters.....	467
9.5.1	Low- and High-Pass Edge Filters.....	467
9.5.2	Band Pass Interference Filters.....	472
9.5.2.1	Narrow-Band Filters.....	472
9.5.2.2	Broad Band Filters.....	476
9.6	Absorptive Coatings.....	477
9.6.1	Eye Protection Coatings.....	477
9.6.2	Photo Masks.....	478
9.6.3	Scales, Reticles, Apertures.....	480
9.6.4	Phase Plates.....	480
9.7	Transparent Conductive Coatings.....	482
9.8	Energy-Related Coatings.....	484
9.9	Solderable Coatings.....	486
9.10	Integrated Optics.....	486
9.10.1	Integrated Optics Components.....	487
9.10.2	Present Status and Trend.....	492
9.11	Scientific Applications.....	496
	References.....	499
	AUTHOR INDEX.....	511
	SUBJECT INDEX.....	539

## CHAPTER 1

### 1. INTRODUCTION AND HISTORY

Glass is the general term for a number of special materials of varying composition and properties. In our time, glass is of considerable importance for the production of scientific, technical, architectural and decorative objects and many articles used in daily life. The material, however, was also very important in former times. Glass has been known since the earliest times in history. Molten minerals containing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$  and  $\text{H}_2\text{O}$  extruded from inside the earth and quickly cooled down formed a natural glass, obsidian. The appearance of this mineral glass is translucent, usually coloured and sometimes also transparent. Worked objects such as spear heads and knives from the Stone Age and obsidian mirrors and objects for ceremonial purposes and jewelry from later periods have been found almost everywhere that the mineral occurs.

When and where glass was first made artificially is an open question. It would appear, however, that it took place in Asia Minor and Egypt about 4500 years ago. Including glazed pottery, it might be more than 7000 years ago.

Glass was used first as a gem and then later for hollow vessels, especially unguent jars and small vases, which were not blown but moulded. The Egyptians used mostly coloured glass with little brilliance because of its low refractive index. Transparent glass was rare and it always contained small bubbles as a consequence of insufficient melting temperatures. For a long period the art of making glass was limited by the primitive firing technique. The development of better glass melting furnaces brought about an improvement in glass quality.

With the invention of glass blowing, which is assumed to have occurred at the beginning of the Christian era, glass objects became more utilitarian than purely decorative and luxurious. About 100 years after the birth of Christ, in Alexandria colourless glass was obtained by the addition of manganese oxide to the glass melt. In the Roman Empire, glass had become a common household material. Besides tableware, toilet bottles and unguent vases, it was also used for storage of wine and other liquids and for seals and signets. The first glass windows are mentioned at the end of the third century. In this period, glass manufacture spread throughout the Empire. After the fall of Rome, glass manufacture was carried on in the Eastern Roman Empire.

In the Islamic world, besides tableware and decorative glass elements, the use of glass for weights was developed to high accuracy by about the year 780 A.D. At the time of the Crusades and after the fall of the Eastern Empire at the beginning of the eleventh century, Venice became famous for glass manufacture. Excellent glasses, the crackled ware and coloured types based on oxide coloration, were made in Murano. The highest point in Venetian glass manufacture at this time was the creation of an

extraordinarily pure crystal glass. Although not invented there, the art of making mirrors with mercury layers was known by about 1369. Glass manufacture spread from Venice to many other European countries in the following centuries and the development of glass was now rapid.

In 1600, the art of cut glass was developed and many beautiful objects were made using this technique. Flint glass, having a higher refractive index and greater dispersive power than the crown glass, as a consequence of lead oxide content, was invented in England in 1675. The invention of gold-ruby glass and the development of a commercial process for the production of such glasses occurred in about 1680.

Progress in glass manufacture during the nineteenth century was made by the use of selected and purified raw materials and the construction of new and better melting furnaces.

New types of glass, known as optical glasses, were created in the glass factories of Germany, England and France. Compared with ordinary glasses, optical glasses are free from physical imperfections and have a wide range of refractive indices and dispersion. Very important studies of the properties of glass as a function of its composition were performed mainly in Germany in about 1890. Art and experience in glass-making were enlarged by scientific knowledge.

The production of hollow and flat glass, however, was still very difficult. The output depended greatly on the skill of the individual workman. More details concerning the history of early glass production can be found in refs. [1-8]. The revolution in glass manufacturing in the twentieth century was and is the trend towards mechanization of the glass industry. The Fourcault process (Belgium, 1905) was the basis for the first machine-drawn plate glass production in 1914 [8]. Some years later, Colburn in the USA invented another drawing method which became known in 1917 as the Libbey-Owens process [8]. The advantages of both older processes were combined in a very rapid new drawing technology used since 1928 and known as the Pittsburgh process (Pittsburgh Plate Glass Company, USA).

Most plate glass was drawn in continuous sheets directly from a melting tank using these processes.

At the beginning of 1960, a completely new and very powerful technology, the float glass process, became famous, replacing extensively the older drawing techniques. It was developed in England by Pilkington Brothers Ltd. [8]. Casting and pressing of glass is also entirely mechanized. The hand process was replaced step by step by machines, leading to today's computer-controlled automatic production plants.

Plastic Materials must be included in the most important inventions of our century. Although plastics differ in chemical composition, method of manufacture and many properties from traditional inorganic glasses, some of them are transparent and in other optical properties similar to glass [9]. Thin foils can be made which are interesting for special applications. Organic glasses offer unique possibilities in design of optical elements [10]. They therefore become more and more a valuable complement to inorganic optical glass.

Finally, it must be stated that there are very few applications of glass in research and industry where the surface properties of the glass can be neglected. Thus the de-

velopment of processes for surface treatments such as grinding, polishing, cleaning and coating has been of immense importance.

There are only few monographs available concerning the properties of glass surfaces [11,12]. Particularly in the case of organic glasses, published data are rare. Marked differences between inorganic and organic materials, however, are one reason for different surface properties. Other factors influencing the nature of a surface, even with the same material, are the various methods used to produce a surface. The success of further surface treatment operations often depends on previous grinding, polishing and cleaning procedures. Proper coating includes all the procedures before film deposition.

Coatings on various glasses are made to produce controlled special variations of their optical, electrical, chemical and mechanical properties. The glass to be coated may have two different functions: it can be an active element (e.g. a lens) or a passive element (e.g. a substrate for an interference filter). The deposited Films may be either functional or decorative in their technical applications.

It is interesting to note that the first antireflection layer on glass was made incidentally 1817 by Fraunhofer [13] in Germany by treating polished glass with concentrated sulphuric or nitric acid. But no technical application was tried at that time.

In 1935 Strong [14] in the USA and Smakula [15] in Germany developed the single layer antireflection coating produced by evaporation and condensation of calcium fluoride under vacuum onto glass surfaces. In 1938 Cartwright and Turner [16] suggested the use of a number of further suitable compounds. The list contained magnesium fluoride and cryolite among other fluorides. Although optically excellent, the mechanical and environmental stability of these coatings was poor. An exception was magnesium fluoride which could be rendered water resistant by baking at high temperature. In 1942, however, in the USA the first stable and abrasion resistant single layer antireflection coating of magnesium fluoride was made by deposition onto previously heated glass by Lyon [17]. After World War II, this material and deposition technique became standard procedure.

Attempts to develop multilayer a.r. coatings had already been made in 1938 in the USA [18] and a little later also in Europe [19]. But a technically satisfactory solution with a double layer system was first achieved in 1949 by Auwärter [20]. The superior quality of this antireflection double layer coating named «Transmax®» (Balzers) caused it to soon be in high demand.

Broadband, triple layer antireflection systems became available in 1965. Film systems could be designed easier and faster by that time with the aid of modern electronic computers.

The industrial development of highly reflective coatings started earlier than that of a.r. coatings. Great enhancement of glass reflectivity can be obtained using high reflecting metal films. Silver mirror films deposited by wet chemical processes were produced before 1835 [21]. The deposition of surface mirror films by the evaporation and condensation of various metals under vacuum was first attempted in 1912 by Pohl and Pringsheim [22]. They used ceramic crucibles as their evaporation sources. Evaporated silver mirrors were also made by Ritschl [23] in 1928. A technically sim-



ple but very effective solution for aluminum evaporation was found by Strong [24] in 1933 who used aluminum loaded helical tungsten filament evaporators, a technique which is still often used today. Mirrors made from aluminum by an evaporation technique are superior to silver in several respects. The reflectivity of aluminum is nearly the same as for silver in the visible, but much higher for the ultra violet [25]. Al mirrors adhere to glass more tenaciously than silver, and when exposed to atmosphere show no tarnish. Other features, such as its uniformity of reflectivity and transmission in the visible make Al films important for many technical and scientific applications. The first aluminized lamp, for instance, was made by Wright [26] at General Electric, USA, in 1937. During that period the first evaporated corrosion resistant and hard rhodium mirrors were also made by Auwärter [27] at W.C. Heraeus GmbH. Such mirrors became important for medical applications. Several years later in 1941 Walkenhorst [28] noticed increase in reflectivity of Al films for the visible with increasing deposition rate. Fast deposition was later also found to be necessary to achieve a high ultra violet reflectance.

At the same time Hass [29] invented the silicon oxide protected aluminum surface mirror. Protection against mechanical damage became important in mirror fabrication with the exception of Al mirrors for astronomical applications. And finally, for use in the near ultra violet range, pure aluminum films have to be protected primarily against degrading oxidation on exposure to air by covering them with layers of MgF, or LiF, as was found out by Hass et al. [30] in the time between 1955 and 1961.

At Schott und Genossen in Germany, Geffcken [31] deposited the first thin film metal dielectric narrow band interference filter of the Fabry-Perot type in 1939; Geffcken also made valuable contributions to the theory of thin film interference systems which were important for the later development of thin film interference system design. The practical realization of environmentally stable complex thin film interference systems, such as e.g. multilayer antireflection coatings, various interference mirror stacks, beam splitters and some high and low pass edge filters require hard and resistant coating materials. Such materials became available in the form of a variety of oxide films which can be easily deposited by the reactive gas deposition process invented by Auwärter [32] in 1952.

From that time there has been very intensive development. This has been concerned primarily with the conception and detailed development in the fields both of computer aided coating design as well as in coating production methods.

In general, coatings are desirable or may even be necessary for a variety of reasons. These include unique optical and electrical properties, materials conservation and economics or the engineering and design flexibility. Weight reduction is important in the automobile industry. Therefore heavy metallic parts such as grills are being replaced with light-weight plastic parts which have been coated with chromium, aluminum and other metals or alloys. Thin films are also used extensively in aluminum-coated plastic foils for heat insulation, decorative and packaging purposes. Another rather new application is to coat glass panes or plastic foils with indium tin oxide films or special cermet films which are used as architectural coatings to improve the energy efficiency and performance of buildings.

For this purpose large, high volume, in-line glass coaters routinely sputter coat sheets of glass up to three meters in width [33]. But also chemical vapour deposition in form of pyrolysis is in use. Sputtering and pyrolysis are still in competition [34].

The capacities of both techniques may range up to some millions of square meters per year.

The hermetically sealing of sensitive surfaces from water vapour is of great practical importance and can be performed to a high degree of effectiveness with thin films. Using polymeric organic coatings of polytetrafluoroethylene and vinylidene chloride the best barriers are achieved with a water vapour transmission rate of only 4.8 g mil/m<sup>2</sup>/24hr. Whereas polymethyl methacrylate has a hundred times greater and cellulose acetate a more than even two hundred times greater value, for comparison.

For flexible packaging applications thin polymer foils are widely used. Generally gas and vapour permeation of such foils is decreased by aluminization. To avoid, however, the opaque appearance of a metal layer for food and medical packaging purposes transparent thin film barrier layers based on vapour deposited oxidic materials like SiO<sub>x</sub> and Al<sub>2</sub>O<sub>3</sub> are often preferred [35-39]. A 120 Å thick SiO<sub>x</sub> coating on a 0,5 mil thick polyethylene terephthalat, PET, foil provides excellent barrier performance of less than 1 g/m<sup>2</sup>/24hrs for water vapour and less than 1 ml/m<sup>2</sup>/24hrs for oxygen [40].

These few examples may illustrate the broad spectrum of possibilities offered by coating glass and plastic with thin films.

It is the aim of this book to review the production and the nature of glass surfaces together with the various film deposition and measuring techniques and to describe the properties of the films. In a last passage a survey is presented about most of the typical technical thin film products.

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## CHAPTER 2

### 2. COMPOSITION, STRUCTURE AND PROPERTIES OF INORGANIC AND ORGANIC GLASSES

The scientific investigation of composition and properties of inorganic glass started in the last century. By comparison, the development of organic glass is just in its early stages. The question of the structure of glass led to a discussion of whether it exists in a microcrystalline or in an amorphous state. From the thermodynamic point of view, all condensed substances at zero temperature in equilibrium conditions should be crystalline. There are, however, also noncrystalline solids in a metastable state. Relaxation times for crystallisation of these solids are extremely long and they therefore remain amorphous in practice. Crystals are rare and their structures are limited in number and can be reduced to only 14 Bravais lattices. The number of possible non-crystalline structural arrangements, however, is infinite. This diversity of the positions of atoms and molecules does not affect their thermodynamic and transport properties. On the whole, disordered structures are macroscopically presented as homogeneous and isotropic media. It is generally assumed today that glass belongs to the predominant non-crystalline solids.

#### 2.1 GLASS-FORMING INORGANIC MATERIALS

The glassy state is known in some elements, notably selenium and tellurium. Selenium also forms glassy mixtures with phosphorus. There are also some semiconductive glasses of compounds like  $\text{As}_2$ ,  $\text{Se}_3$ . A number of salts may exist as glass. The best known is  $\text{BeF}_2$ . Complex types of glass have been prepared containing  $\text{BeF}_2$  together with  $\text{NaF}$ ,  $\text{KF}$ ,  $\text{LiF}$ ,  $\text{CaF}_2$ ,  $\text{MgF}_2$  and  $\text{AlF}_3$ . Some nitrates ( $\text{Na}$ ,  $\text{K}$ ), sulfates and chlorides have been obtained as small glassy droplets by spraying the molten material onto cold plates. More details on such glasses can be found in ref. [1]. Most of these types of glass, however, have little technical significance. This is not true of the glassy metals. Amorphous alloys or metallic glass containing two or three components such as  $\text{PdSi}$ ,  $\text{FeB}$ ,  $\text{TiNi}$ ,  $\text{NiPB}$  etc., are new materials that have interesting mechanical and magnetic properties that are highly desirable in modern technical applications. They are produced in the form of strips by quenching the melt extremely rapidly [2]. The most important material termed as glass is formed, however, by oxides [1,3,4].

The central difference between metallic, semiconductive and oxide glasses lies in the relative strengths of their chemical bonds as measured by the energy gap between occupied and unoccupied electronic states. In oxide glasses this gap is more than 5 electron volts, that is, it lies in the vacuum ultraviolet so that such glasses are transpar-

ent and colourless, apart from impurities. The semiconductive glasses have energy gaps near 1,5 eV and are coloured yellow or red, while in metallic glasses the energy gap is zero.

Typical and possible glass-forming oxides are listed in Table 1.

TABLE 1  
GLASS-FORMING OXIDES

Typical glass formers:	B <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>
	As <sub>2</sub> O <sub>3</sub>	GeO <sub>2</sub>	As <sub>2</sub> O <sub>3</sub>
	Sb <sub>2</sub> O <sub>3</sub>		
Possible glass formers:	Bi <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>

Silica is the constituent material in technical glass. Commercial glass is almost exclusively silicate glass. Oxides that apparently do not form glass but may be included in glass to obtain special properties such as chemical durability, low electrical conductivity, high refractive index and dispersion, increase in hardness and melting point, etc. are listed in Table 2. To obtain glass that transmits infrared, some special components such as As<sub>2</sub>S<sub>3</sub> and TeO<sub>2</sub>, are used [5].

TABLE 2  
GLASS-PROPERTY-MODIFYING OXIDES

Na <sub>2</sub> O	ZnO	Al <sub>2</sub> O <sub>3</sub>	SnO <sub>2</sub>
K <sub>2</sub> O	BeO	La <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
Pb <sub>2</sub> O	PbO	Y <sub>2</sub> O <sub>3</sub>	ThO <sub>2</sub>
Cs <sub>2</sub> O	MgO	In <sub>2</sub> O <sub>3</sub>	
	CaO		
	CrO		
	SrO		
	BaO		
	CdO		

In term of bond strength between the cation and the oxygen all glass formers have values greater than 5 eV and the typical modifiers have lower values in the range of about 2.8 eV [6].

2.1.1 CRYSTALLITE THEORY

When cooling down from the melting point, many materials pass through a temperature range in which the liquid becomes unstable with respect to one or more crystalline compounds. An increase in viscosity, however, may partially or completely prevent the discontinuous change into the crystalline phase. Studies of refractive index changes by heat treatment and investigations of other physical properties of glass led Lebedev [1,4,7] to the conclusion that glass contains ordered zones of small crystallites.