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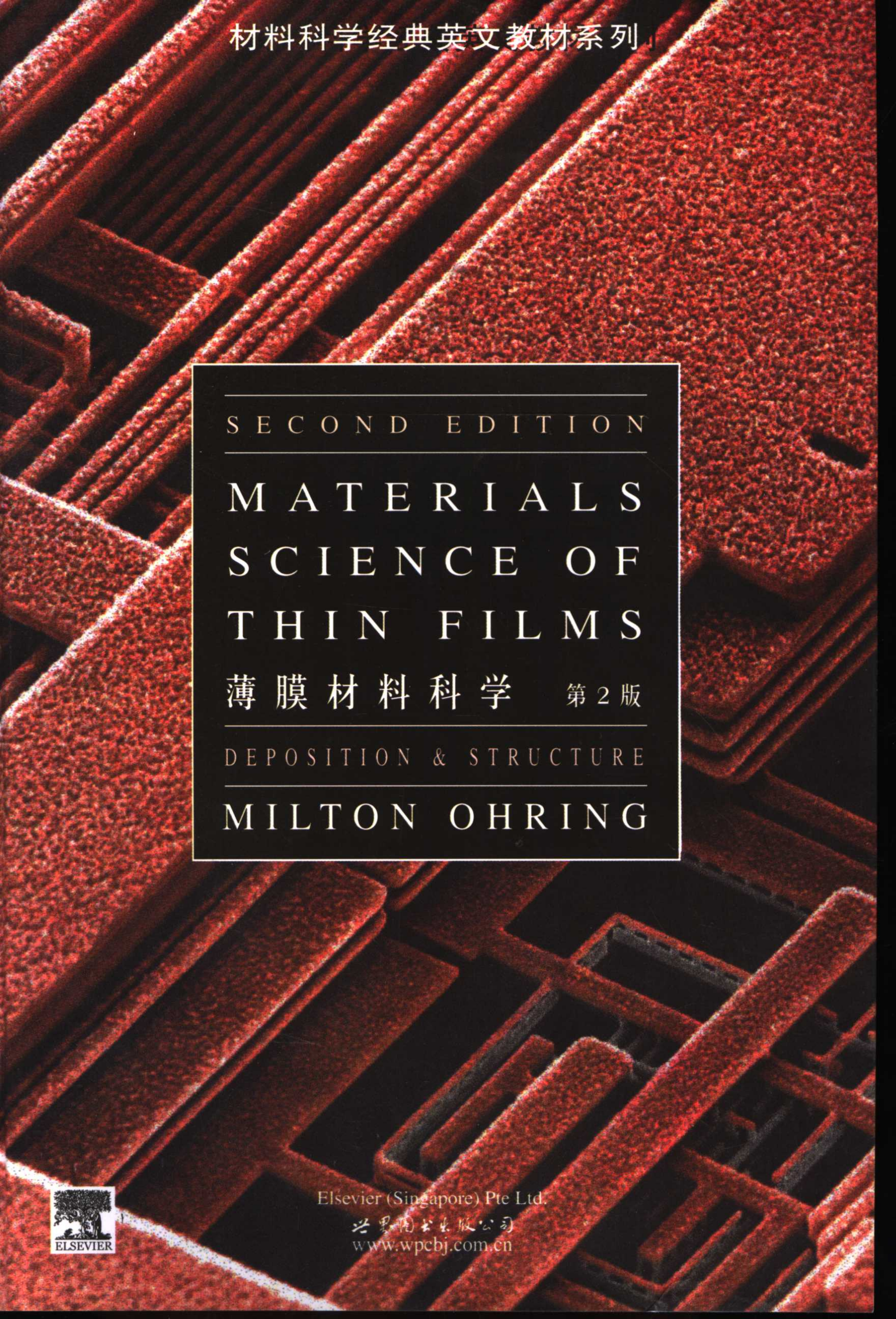

SECOND EDITION

MATERIALS SCIENCE OF THIN FILMS

薄膜材料科学 第2版

DEPOSITION & STRUCTURE

MILTON OHRING

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Materials Science of Thin Films

Deposition and Structure

Second Edition

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Foreword to First Edition

It is a distinct pleasure for me to write a foreword to this new textbook by my long-time friend, Professor Milt Ohring.

There have been at least 200 books written on various aspects of thin film science and technology, but this is the first true textbook, specifically intended for classroom use in universities. In my opinion there has been a crying need for a real textbook for a long time. Most thin film courses in universities have had to use many books written for relatively experienced thin film scientists and engineers, often supplemented by notes prepared by the course instructor. *The Materials Science of Thin Films,* a true textbook, complete with problems after each chapter, is available to serve as a nucleus for first courses in thin film science and technology.

In addition to his many years of experience teaching and advising graduate students at Stevens Institute of Technology, Professor Ohring has been the coordinator of an on-premises, M.S. degree program offered by Stevens at the AT&T Bell Laboratories in Murray Hill and Whippany, New Jersey. This ongoing cooperative program has produced over sixty M.S. graduates to date. Several of these graduates have gone on to acquire Ph.D. degrees. The combination of teaching, research, and industrial involvement has provided Professor Ohring with a broad perspective of thin film science and technology and tremendous insight into the needs of students entering this exciting field. His insight and experience are quite evident in this textbook.

John L. Vossen (1991)

Preface

Technological progress and scientific advances often proceed with different time constants. While the former is often shorter than the latter, they nevertheless march forward in a coupled rhythm. This is perhaps nowhere better illustrated than in thin-film science and technology. And that is why even though much of the subject matter of this book has been dramatically updated, its spirit has remained that of the first edition of *The Materials Science of Thin Films*, which appeared a decade ago. Documenting and interpreting the remarkable technological progress of the intervening years in terms of the underlying, largely unchanging physical and chemical sciences remains an invariant feature of this revised edition.

Thin-film microelectronics and optoelectronics industries are among the strongest technological drivers of our economy, a fact manifested by the explosive growth in communications, and information processing, storage, and display applications. Fruits of these technologies have fertilized expanding thin-film uses in diverse areas, e.g., coatings of all kinds (optical, decorative, environmental, and wear resistant), biotechnology, and the generation and conservation of energy. Common to this family of related thin-film applications are issues rooted in materials science and engineering, accounting for the book's flavor and focus. Included among its pages is an information and knowledge base intended for the same interdisciplinary and varied audience served by the first edition, namely,

1. Science and engineering students in advanced undergraduate or first-year graduate level courses on thin films

2. Participants in industrial in-house courses or short courses offered by professional societies
3. Mature scientists and engineers switching career directions who require an overview of the field

Readers should be reasonably conversant with introductory college chemistry and physics and possess a passive cultural familiarity with topics commonly treated in undergraduate physical chemistry and modern physics courses. Short of this, a good course in materials science and engineering will do. Such courses traditionally focus on bulk solids, typically utilizing metals, semiconductors, ceramics, and polymers, taken singly or collectively as illustrative vehicles to convey principles. The same spirit is adopted in this book, except that thin solid films are the vehicle. Of the tetrahedron of processing–structure–properties–performance interactions, the multifaceted processing–structure concerns are the ones this book primarily focuses on. Within this context, I have attempted to weave threads of commonality among seemingly different materials, processes, and structures, as well as draw distinctions when they exhibit outwardly similar behavior. In particular, parallels and contrasts between films and bulk materials are themes of recurring discussions.

An optional introductory review chapter on standard topics in materials science establishes a foundation for subsequent chapters. Following a second chapter devoted to vacuum science and technology, the remaining text is broadly organized into three sections. Chapters 3, 4, 5, and 6 deal primarily with the principles and practices of *film deposition* from the vapor phase by physical and chemical methods. The increasing importance of plasmas and ion beams in recent years to deposit, etch, and modify films, is reflected in the content of the middle two of these chapters. *Film structure* is the subject of Chapters 7, 8, and 9. These three chapters track the events that start with the condensation of atomic clusters on a bare substrate, continue with film growth due to additional deposition, and end with fully developed polycrystalline, single-crystal (epitaxial), or amorphous films and coatings. Thin films are structurally and chemically characterized by the assorted electron and scanning probe microscopies as well as surface analytical techniques that are described in Chapter 10. Finally, the last two chapters broadly expose the underlying connections between film deposition and structure by addressing the roles of mass transport and stress. These chapters also consider the stability of film systems under driving forces that promote structural and chemical change. Exercises of varying difficulty are provided in each chapter, and I believe a deeper sense of the subject matter will be gained by considering them. Three elegant problems (exercises 5, 6, and 7 of Chapter 12) were developed by Professor W. D. Nix, and I thank him for their use.

I have been most gratified by the reception of the first edition of my book. The present version has been thoroughly revised and no former chapter has remained untouched. Obsolete and unsuitable material has been updated and replaced not only in response to advances in the field, but also to make it better conform to pedagogical demands. In this vein, the last 11 chapters may be viewed as core subject matter applicable to all films and coatings, and therefore suitable for introductory courses. Based on my own experience, I have only been able to present a representative portion, but by no means all aspects, of this core material in a one-semester course on thin films. Former readers will note the omission of chapters dealing with electrical, magnetic, and optical film properties and applications, which were included in the first edition. Because these topics tend to be too specialized for the target audience, time limitations have generally meant their exclusion from course syllabi. Readers interested in these subjects will, however, find a rich but broadly dispersed literature on these subjects.

Because of its emphasis on immutable concepts, I hope this book will be spared the specter of rapid obsolescence. However, if this book will in some small measure help spawn new technology that renders it obsolete, it will have served a useful function.

Acknowledgments

I would like to pay tribute to John Vossen's memory for the advice and steadfast encouragement he provided during the writing of the first edition of this book. His influence extended to this edition as well as through the generous gift of much of his personal library on thin film science and technology to me by his widow Joan. These books, together with the John Vossen Laboratory for Vacuum and Thin Film Technology, established at Stevens Institute by the BOC Corp. and Dr. Abe Belkind, its director, have helped to considerably enhance my awareness and knowledge of plasma processing of thin films. In this regard I am particularly grateful to Abe for carefully reviewing the chapters devoted to physical vapor deposition. However, I am solely responsible for the residual errors and holes in my understanding of this and other subject matter treated in the book.

As with the first edition, this book would not have been possible without the wonderfully extensive intellectual (i.e., human) and physical (i.e., library) resources of Bell Laboratories–Lucent Technologies both at Murray Hill and Whippany. Dale Jacobson should be singled out for his continuous help with many aspects of this book. I thank him as well as Rose Kopf and Al Tate, all of Bell Labs, for both large and small favors. The legacy of past and present members of Bell Labs (acknowledged in the first edition), and the spirit of the wonderful students in the Stevens Institute of Technology–Bell Labs "On Premises Approved Program (OPAP)," who originally planted the seed for a textbook on thin films, lives on in this book. That is why I would like to thank them collectively once again.

I am grateful to my dear friend Bob Rosenberg of the IBM T. J. Watson Research Center for introducing me to the field of thin films and its reliability implications more than three decades ago, and thank him for helping me to gather research publications and key figures for this edition. Helpful comments, discussions, graphics, research papers, and encouragement provided by IBM staff members J. C. M. Harper, S. Rossnagel, R. B. Laibowitz, L. Gignac, D. Gupta, F. M. Ross, and K. P. Rodbell are sincerely appreciated.

I also want to thank a group of colleagues, reviewers, and kind readers, too numerous to acknowledge individually, for sending me research preprints and reprints, for pointing out errors in the text and exercises, and for generally expressing an interest in my efforts. Some special people at Stevens played varied but important roles that enabled this book to reach fruition. They include Dick Widdicombe, Brian Moriarty, Justin Meyer, Pat Downes, Diane Gioia, and Professors Ed Whitakker, Wayne Carr, Kurt Becker, Henry Du, Matt Libera, Steve Bloom, and Bernie Gallois; I appreciate their help at critical moments. Lastly, I am indebted to the team of Peggy Flanagan, Marsha Filion, and Julio Esperas at Academic Press for guiding this project to completion.

Perhaps the greatest gift in life is joy from one's children. That is why this book is dedicated to my children Avi, Noam, and Feigel, and their children Jake, Max, Geffen, and Ami.

Historical Perspective

Thin-film technology is simultaneously one of the oldest arts and one of the newest sciences. Involvement with thin films dates to the metal ages of antiquity. Consider the ancient craft of gold beating, which has been practiced continuously for at least four millenia. Gold's great malleability enables it to be hammered into leaf of extraordinary thinness while its beauty and resistance to chemical degradation have earmarked its use for durable ornamentation and protection purposes. The Egyptians appear to have been the earliest practitioners of the art of gold beating and gilding. Many magnificent examples of statuary, royal crowns, and coffin cases that have survived intact attest to the level of skill achieved. The process involves initial mechanical rolling followed by many stages of beating and sectioning composite structures consisting of gold sandwiched between layers of vellum, parchment, and assorted animal skins. Leaf samples from Luxor dating to the Eighteenth Dynasty (1567–1320 B.C.) measured 0.3 microns in thickness (Ref. 1). As a frame of reference for the reader, a human hair is about 75 microns in diameter. Such leaf was carefully applied and bonded to smoothed wax or resin-coated wood surfaces in a mechanical (cold) gilding process. From Egypt the art spread as indicated by numerous accounts of the use of gold leaf in antiquity.

Today, gold leaf can be machine-beaten to 0.1 micron and to 0.05 micron when beaten by a skilled craftsman. In this form it is invisible sideways and quite readily absorbed by the skin. It is no wonder then that British gold beaters were called upon to provide the first metal specimens to be observed in the transmission electron microscope. Presently, gold leaf is used to decorate such diverse structures and objects as statues, churches, public buildings, tombstones, furniture, hand-tooled leather, picture frames, and, of course, illuminated manuscripts.

Thin-film technologies related to gold beating, but probably not as old, are mercury and fire gilding. Used to decorate copper or bronze statuary, the cold mercury process involved carefully smoothing and polishing the metal surface, after which mercury was rubbed into it (Ref. 2). Some copper dissolved in the mercury, forming a very thin amalgam film that left the surface shiny and smooth as a mirror. Gold leaf was then pressed onto the surface cold and bonded to the mercury-rich adhesive. Alternately, gold was directly amalgamated with mercury, applied, and the excess mercury was then driven off by heating, leaving a film of gold behind. Fire gilding was practiced well into the 19th century despite the grave health risk due to mercury vapor. The hazard to workers finally became intolerable and provided the incentive to develop alternative processes, such as electroplating (Ref. 3).

Distinct from these physical gold-beating and gilding processes are chemical recipes for decorating copper-base alloy objects with gold-rich coatings. One such technique known as depletion gilding capitalizes on the fact that copper oxidizes preferentially relative to gold. Starting with a relatively dilute copper–gold alloy (*tumbaga*), successive thermal oxidations each followed by dissolution of the resultant copper oxide leaves the surface increasingly enriched in gold. Depletion gilding (Ref. 4) of sheet metals was practiced by the Andean metalsmiths of the Peruvian coast for perhaps two millenia prior to the Spanish conquest of the Incas. Much to the surprise of the Conquistadors when they melted Inca treasure, the bullion contained less gold than originally imagined; a gold-rich veneer only 0.5 to 2 microns thick masked the more plentiful, but relatively worthless copper-rich metal underneath.

The history of gold beating and gilding is replete with experimentation and process development in diverse parts of the ancient world. Practitioners were concerned with the purity and cost of the gold, surface preparation, the uniformity of the applied films, adhesion to the substrate, reactions between and among the gold, mercury, copper, bronze (copper–tin), etc., process safety, color, optical appearance, durability of the final coating, and competitive coating technologies. As we shall see in the ensuing pages, modern thin-film technology addresses these same generic issues, albeit with a great compression of time. And although science is now in the ascendancy, there is still much room for art.

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