MATERIALS SCIENCE

Donglu Shi (Ed.)

Functional Thin Films and Functional Materials

New Concepts and Technologies

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功能薄膜与功能材料

——新概念与新技术

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内 容 简 介

本书是海内外在功能薄膜研究领域有重要建树的专家和学者合作的结晶。本书共分九章。重点介绍功能薄膜的物理性质、结构、合成方法、相图、缺陷分析和它们的最新应用。全书内容包括薄膜在分子筛方面的应用，铁电薄膜的新合成方法，纳米薄膜的新结构以及陶瓷中的纤维结构和强度。书中对最新的电镜分析方法作了详细的介绍，这些新方法主要是针对新材料中发现的特殊结构和缺陷建立的。最后一章介绍薄膜结构的计算机数字模拟，重点介绍了有限元法和边界元法的特点以及在某些特殊问题上的应用。

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21 世纪科技前沿丛书
Frontiers of Science and Technology for the 21st Century

《Frontiers of Science and Technology for the 21st Century》

FOREWORD

Over the next several years, Tsinghua University Press will publish a series of books addressing progress in basic sciences and innovations in technology. We have made no attempt to pursue a comprehensive coverage of all disciplines of science and technology. Rather, topics for this series were selected with an emphasis on the currently active forefront of science and technology that will be contemporary in the next century. Most books in this series will deal with subjects of cross disciplines and newly emerging fields. Each book will be completed by individual authors or in a collaborative effort managed by an editor(s), and will be self-consistent, with contents systematically focused on review of the most recent advances and description of current progresses in the field. Sufficient introduction and references will be provided for readers with varying backgrounds. We have realize clearly the challenge of encompassing the diverse subjects of science and technology in one series. However, we hope that, through intensive collaboration between the authors and editors, high standards in editorial quality and scientific merit will be maintained for the entire series.

The international collaboration on this series has been coordinated by the Association of Chinese Scientists and Engineers-USA(ACSE). In the science community, authors voluntarily publish their results and discoveries in the full conviction that science should serve human society. The editors and authors of this series share this academic tradition, and many of them are fulfilling a spiritual commitment as well. For our editors and authors who were graduated from universities in China and further educated abroad in science and engineering, this is an opportunity to dedicate their work to the international education community and to commemorate the historical open-door movement that began in China two decades ago. When the human society enters the

information age, there is no geographic boundary for science. The Editorial committee hopes that this series will promote further international collaboration in scientific research and education at the dawn of the new century.

The Editorial Committee
1999.6

《21 世纪科技前沿》

丛 书 序 言

由清华大学出版社出版的这套丛书是基础科学和应用科学领域内的专门著作。除了可作为研究生教材外，也可作为科研和工程技术人员的参考书。在丛书的题材选择中，着重考虑目前比较活跃而且具有发展前景的新兴学科。因此，这套丛书大都涉及交叉和新兴学科的内容。编写的方式大多由主编策划并组织本学科有影响的专家共同执笔完成，从而使每一本书的系统性和各章节内容的连贯性得到了充分的兼顾。丛书涵盖学科的最新学术进展，兼顾到基本理论和新技术、新方法的介绍，并引入必要的导论和充分的参考文献以适应具有不同学术背景的读者。编撰一套容纳多学科的科技丛书是一项浩繁的工作，我们希望通过主编和作者的集体努力和精诚协作，使整套丛书的学术水准能够保持在较高的水平上。

编辑《21 世纪科技前沿》丛书是由“旅美中国科学家工程师协会”发起的一项国际科技界的合作。传递信息，加强交流，促进新世纪的科技繁荣是编著者们参与此项工作的共同信念。此外，这套丛书还具有特别的纪念意义。20 年前，历史的进程使成千上万的中国学生、学者有机会走出国门，到世界各地学习和从事科学研究。今天，活跃在世界科技前沿领域的中华学子们没有忘记振兴祖国科技教育事业的责任和推动国际学术交流与合作的义务。正是基于这一共同的心愿，大家积极参与这套系列丛书的撰写、组稿和编辑工作。为此，我们愿以这套丛书来纪念中国改革开放 20 周年。

编 委 会

1999.6

Preface

In recent years, industrial applications have rapidly expanded the functional thin films into many new areas including membranes, optical devices, and microwave components in telecommunications. These applications typically employ materials with unique electronic, magnetic, acoustic, and thermal properties. Research on these emerging materials requires an extensive background in physical principles and characterization methods. The challenge for materials researchers is therefore to develop new technologies that can synthesize novel structures and characterize their corresponding unique properties. To achieve such a goal, research must be integrated with current trends in technological development and industrial needs, and must stimulate the interest of interdisciplinary groups.

We intend this book to provide an up-to-date introduction to the field of functional thin films with newly developed technologies and fundamental new concepts. The focus of the book is on the critical areas of novel thin films such as physical properties, structure, synthesis, phase equilibria, defect characterization, and novel applications. An important aspect of the book lies in its wide coverage of practical applications. Not only are the cutting-edge technologies in modern industry introduced, but also unique applications in many rapidly advancing fields. This book is written for a wide readership including university students and researchers from diversified backgrounds such as physics, materials science, engineering, and chemistry. Both undergraduate and graduate students will find it a valuable reference book on key topics related to solid state and materials science. It can also provide frontier researchers most up-to-date information on functional thin films, including novel syntheses methods, unique properties, and new applications.

The book devotes two chapters (Chaps. 1 and 2) to sol-gel science and technology. In these chapters, the authors address the most critical issues in membrane thin films from the perspectives of synthesis, structure, chemistry,

and their unique applications. For instance, in the first chapter, the authors discuss in detail the advantages of polymer membranes in commercial applications. Compared with inorganic membranes, the polymer films can be fabricated in large quantities and with a desired geometry such as sheet, tube or hollow fiber. On the other hand, inorganic materials lack mechanical and fabricating flexibility, so that problems arise involving difficulty in housing, limited packing density relating to membrane area and higher cost. Many applications of organic membranes are introduced including microfiltration and ultrafiltration. The second chapter describes sol-gel synthesis and properties of several major ceramic adsorbents/catalysts or their support bodies for use in chemical reaction and adsorption processes. Nano-structured γ-alumina, zirconia and titania with uniform pore size distribution and an average pore diameter of about 3 nm are prepared by hydrolysis and condensation of corresponding metalorganic precursors. Experimental results on adsorption of ethylene and ethane and sulfation reaction on the sol-gel derived CuCl/alumina and CuO/alumina granules are reported to illustrate the advantages of the sol-gel derived adsorbents/catalysts as compared to those prepared by the conventional methods.

Chapters 3 and 4 focus on the fundamental concepts, novel synthesis methods, unique structures and properties of ferroelectric thin films. These chapters provide a brief summary of the current fundamental understanding of ferroelectricity and ferroelectrics and address critical material issues. One of the most actively pursued ferroelectric applications is highlighted: ferroelectric thin films for digital information storage as dynamic random access memories and non-volatile random access memories. The attention is mainly focused on three types of materials: barium strontium titanate, lead zirconate titanate, and strontium bismuth niobate tantalate, and on major thin film deposition processes including: sputtering, pulsed laser ablation deposition, chemical vapor deposition, liquid injection or mist, metal-organic decomposition, chemical solution deposition, and hybrid deposition processes. The challenges and current approaches are discussed.

Chapters 5 and 6 deal with nanostructured thin films and the mechanical behavior of fiber bridging in a ceramic matrix. They describe composite thin films with many unusual physical properties, which are not realizable with the pure single constituents. In recent years, ultrafine nanocrystalline materials have shown novel physical, chemical, magnetic, optical and electronic properties. Some interesting phenomena such as non-linear optical behavior and quantum confinement effects of carriers have also been reported in nanocomposite materials. Nanocrystalline and nanocomposite materials are believed to play an important role in explaining some fundamental physical problems, such as microstructural and property transitions between the molecular and bulk solid state and also may have technological applications in the future in structural engineering, optoelectronic devices, catalysts for chemical reactions, magnetic

storage and optical coatings.

Chapters 7 and 8 are devoted to techniques developed recently in electron diffraction for the characterization of functional materials. They give details of sample preparation, diffraction principles, experimental procedures, and special methods for critical defect structure analysis. These chapters present many new characterization techniques using transmission electron microscopy. With these highly advanced techniques, defect structures including tweeds, twin boundaries, grain boundaries, stacking faults, and dislocations in a variety of materials are studied in detail.

Chapter 9 should be of most interest to researchers in computer simulation of novel structures and materials. This chapter gives detailed descriptions of novel methods in analyzing internal stresses in functional thin films. In this chapter, two main numerical simulation methods, namely, the finite element method (FEM) and the boundary element method (BEM) for macromechanical, and especially micromechanical analyses of various advanced materials, will be reviewed. Then the chapter will focus on the BEM approach, which offers many advantages over the FEM approach regarding the accuracy and efficiency for certain problems. The BEM formulations will be presented and some special issues associated with the BEM as applied to materials simulations will be addressed. Applications of the BEM to the micromechanical analysis of fiber-reinforced composites with the presence of the interphases and interfacial stress analysis of thin films and coatings will be presented.

We hope these chapters will provide timely and useful information for the progress of functional thin films and applications. We are grateful to all invited authors for their excellent contributions to this book.

Donglu Shi
Cincinnati
October 2001

前 言

最近几年，功能薄膜在工业界的应用已经发展到许多新的领域，包括光学器件以及无线电通信中的微波元件。这些应用技术的实现大多涉及材料的物理性质，例如电性、磁性、声学性质和热学性质。因此，研究这些新型材料时，就要求研究者对材料的基本物理性质以及它们的测定方法有深刻的了解。另一方面，新材料的不断发现以及对它们最新特性的分析和测定又对研究者们提出了新的挑战。为了达到这一目的，当今的研究必须是跨学科的，而且必须满足对工业与技术的各种要求。

本书的目的是向读者提供功能薄膜领域里的一些最新的发展信息。其中着重介绍关键课题中的一些主要内容，例如物性、结构、合成、相图、缺陷分析和最新应用。本书很重要的特点是广泛介绍了功能薄膜的应用，不仅包括最新技术而且有特殊应用的资料。本书为大学生与科研工作者而写。大学生与研究生可把它当作很有价值的参考书，而研究者们则会发现本书中大量的关于功能薄膜方面的最新信息。

本书共有 9 章。第 1 和第 2 章主要介绍有机溶胶的科学与技术。在这两章中，作者详细介绍了有机溶胶法制做薄膜的工艺方法以及对这些薄膜性能的研究。例如，在第 1 章中，作者讨论有机分子筛在商业应用中的优点。与无机分子筛相比，有机薄膜更易于做成不同的几何形状，也可以大批量生产。另一方面有机薄膜比无机薄膜更具有可塑性和高强度，而且比无机薄膜成本低。许多有机薄膜的应用在第 1 章中都做了详细的介绍。第 2 章主要讨论陶瓷薄膜在吸收体与催化剂方面的应用以及它们的合成与性质，并讨论了一些典型陶瓷薄膜内孔洞的分布和相关的性质。

第 3 和第 4 章的重点是铁电薄膜的基本概念、制备方法、结构与性质。这两章提供了该领域中关于铁电材料与铁电性质方面最新的研究进展资料和数据，并详细介绍了铁电薄膜中一些主要的最新应用，例如数字存储、无序记忆等等，一些最典型的铁电薄膜的制备方法也做了详细的介绍。

第 5 和第 6 章主要讨论纳米薄膜和纤维强化的结构陶瓷体。近几年来，纳米薄膜已展现出一些特有的最新性质，比如非线性光学特性以及量子效应。纳米材料在材料科学中将会具有极为重要的地位。这包括发展最新型的工程结构、光电器件、化学催化剂、磁存储和光镀层等等。

第 7 和第 8 章将为读者提供在材料电镜分析方面的最新发展。在样品制备、衍射原理、实验步骤和特殊方法上都做了详细的介绍。这两章还提供了电子显微镜学发展的最新技术和概念，对一些典型的缺陷如孪晶、晶界、层错和位错的最新电镜分析方法都做了一一介绍。

第 9 章着重介绍薄膜结构的计算机数值模拟，讲述了两种主要的模拟方法——有限元法和边界元法。本章着重讨论了这两种方法的特点以及在某些特殊问题上的应用。例如，用边界元法对在薄膜应力分析上的应用做了详细的介绍。

我们希望本书能为读者们提供在功能薄膜领域中的最新信息，我们也在此衷心地感谢所有作者对本书的重要贡献。

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