CERAMIC FILMS AND COATINGS

Edited by

John B. Wachtman and Richard A. Haber

The Center for Ceramics Research
Rutgers, the State University of New Jersey
Piscataway, New Jersey

NOYES PUBLICATIONS
Park Ridge, New Jersey, U.S.A.

Library of Congress Catalog Card Number: 92-540
ISBN: 0-8155-1318-6
Printed in the United States

Published in the United States of America by
Noyes Publications
Mill Road, Park Ridge, New Jersey 07656

10 9 8 7 6 5 4 3 2 1

Library of Congress Cataloging-in-Publication Data

Ceramic films and coatings/edited by John B. Wachtman, Richard A. Haber.
p. cm.
Includes bibliographical references and index.
ISBN 0-8155-1318-6
1. Ceramic coating. 2. Thin films. I. Wachtman, J.B., 1928- II. Haber, Richard A., 1960-
TS695.9.C46 1992
667'.9--dc20 92-540
CIP

MATERIALS SCIENCE AND PROCESS TECHNOLOGY SERIES

Editors

Rointan F. Bunshah, University of California, Los Angeles *(Series Editor)*
Gary E. McGuire, Microelectronics Center of North Carolina *(Series Editor)*
Stephen M. Rossnagel, IBM Thomas J. Watson Research Center *(Consulting Editor)*

Electronic Materials and Process Technology

DEPOSITION TECHNOLOGIES FOR FILMS AND COATINGS: by Rointan F. Bunshah et al

CHEMICAL VAPOR DEPOSITION FOR MICROELECTRONICS: by Arthur Sherman

SEMICONDUCTOR MATERIALS AND PROCESS TECHNOLOGY HANDBOOK: edited by Gary E. McGuire

HYBRID MICROCIRCUIT TECHNOLOGY HANDBOOK: by James J. Licari and Leonard R. Enlow

HANDBOOK OF THIN FILM DEPOSITION PROCESSES AND TECHNIQUES: edited by Klaus K. Schuegraf

IONIZED-CLUSTER BEAM DEPOSITION AND EPITAXY: by Toshinori Takagi

DIFFUSION PHENOMENA IN THIN FILMS AND MICROELECTRONIC MATERIALS: edited by Devendra Gupta and Paul S. Ho

HANDBOOK OF CONTAMINATION CONTROL IN MICROELECTRONICS: edited by Donald L. Tolliver

HANDBOOK OF ION BEAM PROCESSING TECHNOLOGY: edited by Jerome J. Cuomo, Stephen M. Rossnagel, and Harold R. Kaufman

CHARACTERIZATION OF SEMICONDUCTOR MATERIALS—Volume 1: edited by Gary E. McGuire

HANDBOOK OF PLASMA PROCESSING TECHNOLOGY: edited by Stephen M. Rossnagel, Jerome J. Cuomo, and William D. Westwood

HANDBOOK OF SEMICONDUCTOR SILICON TECHNOLOGY: edited by William C. O'Mara, Robert B. Herring, and Lee P. Hunt

HANDBOOK OF POLYMER COATINGS FOR ELECTRONICS—Second Edition: by James J. Licari and Laura A. Hughes

HANDBOOK OF SPUTTER DEPOSITION TECHNOLOGY: by Kiyotaka Wasa and Shigeru Hayakawa

HANDBOOK OF VLSI MICROLITHOGRAPHY: edited by William B. Glendinning and John N. Helbert

CHEMISTRY OF SUPERCONDUCTOR MATERIALS: edited by Terrell A. Vanderah

CHEMICAL VAPOR DEPOSITION OF TUNGSTEN AND TUNGSTEN SILICIDES: by John E.J. Schmitz

ELECTROCHEMISTRY OF SEMICONDUCTORS AND ELECTRONICS: edited by John McHardy and Frank Ludwig

(continued)

HANDBOOK OF CHEMICAL VAPOR DEPOSITION: by Hugh O. Pierson

DIAMOND FILMS AND COATINGS: edited by Robert F. Davis

ELECTRODEPOSITION: by Jack W. Dini

Ceramic and Other Materials—Processing and Technology

SOL-GEL TECHNOLOGY FOR THIN FILMS, FIBERS, PREFORMS, ELECTRONICS AND SPECIALTY SHAPES: edited by Lisa C. Klein

FIBER REINFORCED CERAMIC COMPOSITES: by K.S. Mazdiyasni

ADVANCED CERAMIC PROCESSING AND TECHNOLOGY—Volume 1: edited by Jon G.P. Binner

FRICTION AND WEAR TRANSITIONS OF MATERIALS: by Peter J. Blau

SHOCK WAVES FOR INDUSTRIAL APPLICATIONS: edited by Lawrence E. Murr

SPECIAL MELTING AND PROCESSING TECHNOLOGIES: edited by G.K. Bhat

CORROSION OF GLASS, CERAMICS AND CERAMIC SUPERCONDUCTORS: edited by David E. Clark and Bruce K. Zoitos

HANDBOOK OF INDUSTRIAL REFRACTORIES TECHNOLOGY: by Stephen C. Carniglia and Gordon L. Barna

CERAMIC FILMS AND COATINGS: edited by John B. Wachtman and Richard A. Haber

Related Titles

ADHESIVES TECHNOLOGY HANDBOOK: by Arthur H. Landrock

HANDBOOK OF THERMOSET PLASTICS: edited by Sidney H. Goodman

SURFACE PREPARATION TECHNIQUES FOR ADHESIVE BONDING: by Raymond F. Wegman

FORMULATING PLASTICS AND ELASTOMERS BY COMPUTER: by Ralph D. Hermansen

HANDBOOK OF ADHESIVE BONDED STRUCTURAL REPAIR: by Raymond F. Wegman and Thomas R. Tullos

CARBON-CARBON MATERIALS AND COMPOSITES: edited by John D. Buckley and Dan D. Edie

Contributors

Christopher C. Berndt
Department of Materials
Science & Engineering
State University of New York
Stony Brook, NY

Robert Caracciolo
ITT Avionics
Clifton, NJ

David G. Coult
AT&T Bell Laboratories
Solid State Technology Center
Breinigsville, PA

Brian D. Fabes
Department of Materials
Science & Engineering
University of Arizona
Tucson, AZ

Edward N. Farabaugh
Materials Science &
Engineering Laboratory
National Institute of
Standards and Technology
Gaithersburg, MD

Albert Feldman
Materials Science &
Engineering Laboratory
National Institute of
Standards and Technology
Gaithersburg, MD

Richard A. Haber
The Center for Ceramics
Research
Rutgers, the State University
of New Jersey
Piscataway, NJ

Thomas E. Hale
Carboloy, Inc.
Warren, MI

Herbert Herman
Department of Materials
Science & Engineering
State University of New York
Stony Brook, NY

Arun Inam
Bellcore
Red Bank, NJ

Frank A. Kuchinski
Technology Partners, Inc.
Landisville, PA

Carl J. McHargue
Metals and Ceramics Division
Oak Ridge National Laboratory
Oak Ridge, TN

Lawrence H. Robins
Materials Science & Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, MD

Daniel J. Shanefield
The Center for Ceramics Research
Rutgers, the State University of New Jersey
Piscataway, NJ

Donald R. Uhlmann
Department of Materials Science & Engineering
University of Arizona
Tucson, AZ

T. Venkatesan
Physics Department
University of Maryland
College Park, MD

Robert W. Vest
Potter Engineering Center
Purdue University
West Lafayette, IN

John B. Wachtman
The Center for Ceramics Research
Rutgers, the State University of New Jersey
Piscataway, NJ

Hougong Wang
Sherritt Gordon Ltd.
Fort Saskatchewan, Alberta
Canada

Xin Di Wu
Physics Department
University of Maryland
College Park, MD

Brian J.J. Zelinski
Department of Materials Science & Engineering
University of Arizona
Tucson, AZ

Preface

Ceramic films and coatings are both active fields of research and widely used areas of technology. The relatively high hardness and inertness of ceramic materials make ceramic coatings of interest for protection of substrate materials against corrosion, oxidation and wear resistance. The electronic and optical properties of ceramics make ceramic films and coatings important to many electronic and optical devices.

This book presents a series of reviews of many of the most active and technically important areas of ceramic films and coatings. The chapters are intended to be useful to a B.S. or higher level person who is not necessarily an expert in the area. The book is introduced by a survey of the uses and methods of preparation of ceramic films and coatings. The following chapters each focus on an area of application of a type of film with outstanding properties. Each chapter typically considers the processing, properties, and applications of the subject area of film technology. Each of these chapters can be read on a stand-alone basis, but groups of chapters are related, as described below, and reinforce each other by providing perspective and alternate viewpoints.

Four chapters focus on coatings used for protection. An example of a field in which ceramic coatings have become indispensable is treated first: coated cutting tools. A related research area of great promise is taken up in the next chapter: creating an in situ wear resistant film by ion implantation. Chemical protection is then considered. A widely used and important area of technology is the use of ceramic enamel films for protection. Incidentally, decorative aspects of such use are of high commercial importance also. Finally in the area of protective films thermal protection is considered. Such films have become essential in many high temperature devices including combustors and parts of jet engines.

A chapter on synthetic diamond films also relates to the use of films for protection of a substrate. However, these films also have many other potential applications for their electronic, thermal, and optical properties. Diamond thin films are still in a stage of rapid advance. The state of the art in controlling their structure and microstructure is summarized.

Several chapters relate to films used for their optical and electronic properties. Inorganic, nonmetallic thin films for microoptic devices are discussed. Electronic thin films are treated from three standpoints. First, electronic films made by an organic precursor route are treated. Second, ceramic thick film technology for insulators, conductors, and special electrical functions is treated. Third, superconducting thin films are treated in a separate chapter. These latter materials present extreme challenges to thin film technology because of the critical importance of achieving a very narrow range of crystal structure and microstructure required to give the best superconducting properties.

Finally, two areas are taken up which cut across thin film technology. Sol–gel preparation techniques offer a wet chemical route to many types of thin films. This approach has many advantages, but also has limitations. The procedures used for sol–gel film making and the types of microstructures that can be achieved are surveyed.

Characterization of thin films is a requirement for research as well as for quality control in production. The major characterization techniques are brought together and their capabilities and limitations are treated in a single chapter.

The editors thank the authors for their perserverance in preparing chapters and updating them in rapidly moving areas (e.g., superconductivity) even as this book was being produced.

Piscataway, New Jersey
September, 1992

John B. Wachtman
Richard A. Haber

Contents

1. CERAMIC FILMS AND COATINGS—AN OVERVIEW 1
John B. Wachtman and Richard A. Haber
1.0 Introduction 1
2.0 Areas of Application of Ceramic Films and Coatings 2
3.0 Processing of Ceramic Films and Coatings 3
4.0 Characterization of Ceramic Films and Coatings . . 6
5.0 Trends in Ceramic Films and Coatings 10
5.1 Diamond Coatings 11
5.2 High Tc Superconducting Ceramic Thin Films . . 11
5.3 The Sol–Gel Method for Making Ceramic Thin Films 12
5.4 Ceramic Thin Films on Cutting Tools 13
5.5 Ceramic Thin Films in Semiconductor Integrated Circuits 13
5.6 Ceramic Thin Films on Architectural and Automotive Glass 14
6.0 Concept of the Present Book 15
Appendix A. List of Abbreviations and Acronyms 16
References 18

2. CVD COATED CUTTING TOOLS 22
Thomas E. Hale
1.0 Introduction 22
2.0 TiC Coatings 23
2.1 CVD Process Conditions for TiC Coatings 24
TiC Deposition Rate 25

TiC Coating—Substrate Interface 26
3.0 TiN Coatings 27
3.1 CVD Process Conditions for TiN Coatings 27
4.0 Al_2O_3 Coatings 28
4.1 CVD Process for Al_2O_3 Coatings 29
5.0 Multi-Layer Coatings 30
5.1 TiN-TiC Type Multi-Layers 31
5.2 Al_2O_3 Layer Multi-Coatings 32
5.3 CVD Processes for Multi-Layer Coatings 33
6.0 Coating Thickness Optimization 33
6.1 Cutting Tool Wear Modes 33
6.2 Influence of Thickness upon Flank Wear Resistance 34
6.3 Thickness Influence on Crater Wear Resistance and Strength 36
6.4 Thickness of Multi-Layer Coatings 36
7.0 Other Coatings 36
7.1 Hafnium and Zirconium Based Coatings 38
Influence of Coating Composition on Machining Performance of Zr/HfCN Coatings 38
Commercial Uses of Zr/Hf Based Coatings . . 38
7.2 TiB_2 Coatings 39
CVD Process for TiB_2 Coatings 39
7.3 Tungsten Carbide Coatings 40
CVD Process Conditions for Tungsten Carbide Coatings 40
References 41

3. WEAR RESISTANT THIN FILMS BY ION IMPLANTATION . . 42
Carl J. McHargue
1.0 Introduction 42
2.0 Wear Processes in Ceramics 44
2.1 Friction 44
2.2 Adhesive Wear 45
2.3 Abrasive Wear 48
2.4 Surface Fracture 48
3.0 Fundamental Processes in Ion-Solid Interactions 49
3.1 Range of Incident Ions 50
3.2 Defect Production and Retention 51
4.0 Ion Implantation of Ceramics 53
4.1 Microstructural and Property Changes in Ion Implantation 54

4.2 Compound Synthesis by Ion Implantation 61
5.0 Ion Beam Mixing 62
6.0 Ion Beam Assisted Deposition 65
7.0 Summary 70
References 71

4. CORROSION RESISTANT THICK FILMS BY ENAMELLING 77
Frank A. Kuchinski
1.0 Introduction to Porcelain Enamels 77
1.1 History of Porcelain Enamelling 78
1.2 Reasons for Porcelain Enamelling 79
1.3 General Applications for Porcelain Enamels 81
2.0 Porcelain Enamelling Principles and Theories 80
2.1 Porcelain Enamel Smelting and Fritting 82
2.2 Metals Selection and Preparation for Porcelain Enamelling 83
2.3 Porcelain Enamel Milling 87
2.4 Porcelain Enamel Application Methods 90
2.5 Porcelain Enamel Bond Theories 92
2.6 Covercoat Opacity Mechanisms 97
2.7 Drying, Firing and Defects in Porcelain Enamels 100
2.8 Other Comments on Materials and Processing 105
3.0 Applications and Improvement Methods for Protective Porcelain Enamel Coatings 105
3.1 Applications and Competitive Coatings 105
3.2 Porcelain Enamel Properties Testing 111
3.3 Enhancement of Porcelain Enamel Protective Properties 115
4.0 Summary 118
References 119

5. PLASMA SPRAYED CERAMIC COATINGS 131
Herbert Herman, Christopher C. Berndt, and Hougong Wang
1.0 Introduction 131
2.0 Plasma Spraying 132
2.1 Feedstock Powders 135
2.2 The Ceramic Coating 136
2.3 Special Features of Plasma-Sprayed Coatings 138
3.0 Alumina-Based Ceramics 139
4.0 Thermal Barrier Coatings 143

4.1 Applications 143
Aero-Engines 144
Diesel Engine Applications 145
Power Generation Plant Applications 149
4.2 Materials Properties 149
Routine Quality Control Tests 149
Mechanical Properties 150
Cyclic Thermal Testing 153
Thermal Expansion Tests 157
Acoustic Emission Tests 158
Overview of TBC's 158
5.0 Plasma Sprayed High Tc Superconductors 160
5.1 Spray Parameter Optimization 161
5.2 Post-Spray Annealing and Improving Superconducting Properties 163
5.3 Texturing: Improving the Transport Critical Current Density 168
5.4 Coating/Substrate Interdiffusion 173
6.0 Test Methodologies 175
6.1 Characteristics of Coatings 175
6.2 Properties of Coatings 177
References 180

6. OPTICAL THIN FILMS 189
David G. Coult
1.0 Introduction 189
2.0 Optical Thin Film Design 190
2.1 Antireflection Coatings 191
2.2 Multilayer Stacks 193
3.0 Thin Film Materials 195
4.0 Deposition Process 197
5.0 Film Properties 201
5.1 Effects of Deposition Conditions 201
5.2 Effects of Film Microstructure 202
6.0 Attempts at Improved Properties 208
6.1 Sputtering Techniques 208
DC Sputtering 210
RF Sputtering 211
Ion Beam Sputtering 212
6.2 Evaporation Techniques 213
Activated Reactive Evaporation (ARE) 213
Ion Plating 213
Ion-Assisted Deposition (IAD) 215
7.0 Conclusion 217

References 217

7. SOL-GEL DERIVED CERAMIC COATINGS 224
Brian D. Fabes, Brian J.J. Zelinski and Donald R. Uhlmann
1.0 Introduction 224
2.0 Sol-Gel Processing 225
2.1 Coating Chemistry 225
Oxides 225
Non-Oxides 228
2.2 Drying and Firing 229
3.0 Coatings via Sol-Gel Processing 231
3.1 Special Solution Requirements 231
3.2 Coating Techniques 232
3.3 Unique Advantages of Sol-Gel Coatings 236
4.0 Applications 237
4.1 Electrical Applications 237
4.2 Optical Applications 242
Antireflection Coatings 242
Planar Waveguides 244
Surface Patterning 245
Colored Coatings and Reflective Coatings . . 250
Electro-Optic Materials 250
Dyes in Gels 254
Electrochromic Films 255
Organic/Inorganic Composites as
Non-Linear Optical Materials 256
5.0 Outstanding Problems 260
5.1 Film Cracking 260
5.2 Removal of Residual Species 263
5.3 Precursor Characterization and Aging 264
5.4 Impact of Deposition Conditions on Film
Properties 264
5.5 Low Temperature Densification of Films 267
5.6 Comparison of Thin Film vs. Bulk Ceramics . . . 268
5.7 The Nature of Sol-Gel Research 268
6.0 Future Directions 269
References 271

8. ELECTRONIC THICK FILM TECHNOLOGY 284
Daniel J. Shanefield
1.0 Introduction 284
1.1 Comparisons to Competing Technologies 286
2.0 Materials 289
2.1 Substrates 289

2.2 Conductors 290
3.0 Resistors 295
4.0 Dielectrics 296
5.0 Capacitors 297
6.0 Future Directions 297
References 300

9. ELECTRONIC FILMS FROM METALLO-ORGANIC PRECURSORS 303
Robert W. Vest
1.0 Introduction 303
1.1 Overview of MOD Technology 303
1.2 Historical Review 305
1.3 Advantages and Limitations 306
2.0 Metallo-Organic Systems 307
2.1 Selection of Compounds 307
2.2 Synthesis of Compounds 311
Neutralization 311
Double Decomposition from Ammonium Soap 311
Double Decomposition from Amine Soap . . 312
Metathesis Reaction from Metal Acetate . . . 313
Metathesis Reaction from Metal Alkoxide . . 314
Metal Amine Carboxylates 314
2.3 Solvent Considerations 315
Requirements 315
Solvency 316
Selection Procedure 320
3.0 Processing 321
3.1 Film Deposition 321
3.2 Pyrolysis 325
3.3 Annealing 330
3.4 Patterning 334
4.0 Examples of MOD Films 336
4.1 Conductor Films 336
Metals 336
Oxides 337
4.2 Resistor Films 338
4.3 Dielectric Films 339
Linear Dielectrics 339
Ferroelectrics 339
5.0 Summary 341
References 343

10. CHEMICAL CHARACTERIZATION TECHNIQUES FOR THIN FILMS 348
Robert Caracciolo
1.0 Introduction 348
2.0 X-Ray Photoelectron Spectroscopy (XPS) 350
2.1 Experimental Considerations 350
2.2 Radiation Sources 353
2.3 Electron Energy Analyzers 354
2.4 The XPS Spectrum 355
2.5 Insulators 355
2.6 Sampling Depth in XPS 357
2.7 The 'Chemical Shift' in XPS 362
3.0 Auger Electron Spectroscopy (AES) 363
3.1 General Theory 364
3.2 Sampling Depth in AES 367
3.3 The Chemical Shift in AES 367
4.0 Backscattering Spectrometry (RBS and ISS) 369
4.1 Kinematics of the Elastic Collision 369
4.2 Energy Loss 370
4.3 Depth Profiles by RBS 371
4.4 Ion Scattering Spectroscopy 374
5.0 Secondary Ion Mass Spectroscopy (SIMS) 374
6.0 Summary 379
References 380

11. HIGH T_c SUPERCONDUCTING THIN FILMS 382
X.D. Wu, A. Inam, T. Venkatesan
1.0 Introduction 382
2.0 Vacuum Deposition 387
2.1 Thermal and Electron Beam Evaporation 387
2.2 Sputtering 390
2.3 Ion Beam Deposition 391
2.4 Pulsed Laser Deposition 392
2.5 Molecular Beam Epitaxy 393
2.6 Chemical Vapor Deposition (CVD) and Organometallic CVD 394
3.0 Non-Vacuum Deposition 395
3.1 Liquid-Phase Epitaxy 395
3.2 Plasma Spray 396
3.3 Solution Method 396
4.0 Comparison of the Thin Film Techniques 396
5.0 Other High T_c Superconductors 399
6.0 Substrate 399
6.1 Lattice Constant 399

6.2 Thermal Expansion Coefficient 401
6,3 Reactivity 401
6.4 Dielectric Constant 401
7.0 Applications 402
Wires and Tapes 402
Electromagnetic Shielding 402
Passive Microwave Components 402
Discrete Devices 402
Interconnection 403
8.0 Conclusion 403
References 404

12. CHEMICAL VAPOR DEPOSITED DIAMOND 413
Albert Feldman, Edward N. Farabaugh, and Lawrence H. Robins
1.0 Introduction 413
2.0 Historical Background 414
3.0 Methods of Deposition 415
4.0 Growth and Quality of CVD Diamond 419
5.0 Thermal Properties of CVD Diamond 427
6.0 Optical Properties 429
7.0 Mechanical Properties 432
8.0 Polishing CVD Diamond 434
9.0 Conclusion 436
References 437

INDEX 442

1

Ceramic Films and Coatings - An Overview

John B. Wachtman and Richard A. Haber

1.0 INTRODUCTION

The processing, study and use of ceramic films and coatings is done by people with various technical backgrounds. The wide range of materials, techniques for preparation and types of application make this an inherently interdisciplinary field. The present general overview attempts to introduce the subject to the worker who is interested in this field but whose expertise is in one of the related disciplines and who is not an overall expert in films and coatings.

Films and coatings are used for an enormous and diverse set of applications including electronic and optical devices (1)-(3)(3a), protection at high temperatures (4), cutting tool enhancement, and large-scale architectural and automotive use (5). Many of these applications require the properties associated with inorganic, nonmetallic materials; i.e., with ceramics.

The special physical properties of ceramics derive from their fundamental bond type (6). Characteristically ceramics are compounds with bonds that are primarily of a mixed ionic/covalent type rather than a metallic type. As a result, most ceramics have completely filled electronic valence bands separated by a wide forbidden band from completely empty electronic conduction bands causing them to be electrical insulators and to be transparent. Because of the availability of the wide range of ceramic compounds and the ability to introduce additives into their structures, their electronic and optical properties can be tailored to make them semiconductors and electro-optic materials useful as wave guides, modulators, and detectors.

Because of the basic bonding and structural features of ceramics, some possess large and useful amounts of ferroelectricity, ferromagnetism, piezoelecticity, and pyroelectricity. Many ceramics have the high bond strength between atoms that leads to great hardness, stiffness and strength. Many also have good resistance to corrosion and oxidation at high temperatures.

The special properties of ceramics lead to a wide range of applications. Continuing reduction in the scale of microelectronics and increases in the complexity of microelectronic devices have greatly extended thin film technology. Lines and other geometric features of one micron lateral scale or less are used. Films are needed for insulators, conductors, and hermetic seals. Integrated optics technology requires sources, transmission lines, modulators, and detectors made by thin film technology.

Development of new materials has affected ceramic film and coating technology. The discovery that multiple layer coatings can have extraordinary mechanical properties including very high values of elastic moduli is one example. The development of procedures for growing true diamond thin films has set off a whole field of research. The discovery of the high Tc superconducting ceramics which have their best properties as highly-oriented thin films has caused intense efforts to process these materials into good thin films and to combine them with normal conductors to make devices.

Modern ceramic film technology has been strongly affected by many lines of progress in related technologies. This progress includes developments in vacuum technology, film processing, film characterization, materials science of ceramics, semiconductor device technology, optical technology, and cutting tool technology. The following sections summarize the major areas of application, discuss the major processing techniques, discuss the major characterization techniques, and give some perspective on exciting trends toward new ceramic films and new applications.

2.0 AREAS OF APPLICATION OF CERAMIC FILMS AND COATINGS

Table 1 gives a brief summary of areas of application with some typical examples of ceramics for each (6). Practical ceramic films vary greatly in function and thickness. Some have been in use for a long time and others are just coming into use. At one extreme are the naturally-forming oxide films which act as the oxidation barrier on stainless steels. These are typically as thin as 10 nm or less. At the other extreme are the porcelain enamel films as thick as 1 mm or more which are used to protect steel from corrosion. There is thus a long-standing ceramic film and coating technology with its roots in practical needs.

Table 1. Uses of Ceramic Films and Coatings (6)

Use	Typical Ceramic Material
Wear Reduction	Al_2O_3, B_4C, Cr_2O_3, Cr B_2 Cr Si_2, Cr_3Si_2, DLC*, Mo_2C $MoSi_2$, SiC, TiB_2, TiC, WC
Friction Reduction	MoS_2, BN, BaF_2
Corrosion Reduction	Cr_2O_3, Al_2O_3, Si_3N_4, SiO_2
Thermal Protection	Ca_2Si_4, $MgAl_2O_4$, MgO, ZrO_2 (Mg or Ca stabilized)
Electrical conductivity	In_2O_3/SnO_2, $YBa_2Cu_3O_{7-x}$
Semiconductors	GaAs, Si
Electrical Insulation	SiO_2
Ferroelectricity	$Bi_4Ti_3O_{12}$
Electromechanical	AlN
Selective optical transmission and reflectivity	BaF_2/ZnS, CeO_2, CdS, CuO/Cu_2O, Ge/ZnS, SnO_2
Optical wave guides	SiO_2
Optical processing (electrooptic, etc.)	GaAs, InSb
Sensors	SiO_2, SnO_2, ZrO_2

* DLC = Diamond-like carbon

3.0 PROCESSING OF CERAMIC FILMS AND COATINGS

It can be argued that most if not all of the current film production techniques are merely extensions of processes already studied more than 50 years ago. Such techniques can be grouped into four categories: *(i)* atomic deposition processes, *(ii)* particulate deposition processes, *(iii)* bulk coating, and *(iv)* surface modification (6). The principal techniques in these categories are listed in Table 2. The degree of extension of these basic techniques in recent decades is so great in many cases that it constitutes a revolution in process control and in the type and quality of films and coatings which can be made. For example, the degree of process control now possible allows the growth of epitaxial layers with desirable properties in many systems (1)(2)(7)-(15). A relatively new process is laser ablation which uses very short-pulse lasers to transfer complex compounds to a substrate with little or no change in composition (8).

Progress in vacuum technology in the 1950s and 1960s made it possible to operate at pressures of 10^{-11} torr instead of the previous limit of about 10^{-6} torr (16). This makes it possible to study the chemistry and structure of surfaces without significant contamination. Also, these vacuum techniques can be used to lower the contamination during film production. Even when the film production process operates at a higher pressure, the background contamination can be kept down.

The interaction of depositing ions with the surface is complex. Takagi (17)(18) has emphasized the importance of the kinetic energy of the depositing ions in affecting the processes which occur. Figure 1 from Takagi shows the range of energy per ion and incident flux density of ions corresponding to characteristic operating conditions for deposition, etching, and implantation. Also shown on the figure are the energy ranges that correspond to significant interactions. He notes that an ion energy of a few hundred eV would be very useful but is difficult to achieve because of the space charge repulsion effect. The technique of ionized cluster beam (ICB) deposition is used to avoid space charge repulsion. In this technique, films are deposited by clusters of 500 - 2000 atoms with a small charge per ion compared to individual ions.

The energy of the deposited ion after it has come to equilibrium with the temperature of the surface is also important. Metastable films can be formed if the temperature is too low. The temperature of the substrate is critical to the crystal structure (or lack of it) and the texture of the film. For example, formation of films of superconducting $Ya_1Ba_2Cu_3O_{7-x}$ with good crystallinity and highly preferred orientation requires both a suitable substrate and a deposition temperature above 600°C as discussed in the chapter on superconducting thin films in this volume (Ch. 11).

Some film processing techniques involve a rapid drop in energy of the atoms just before and just after attachment to the substrate. Non-equilibrium phases, both metastable crystalline phases and amorphous phases, can be formed. These typically remain frozen up to temperatures