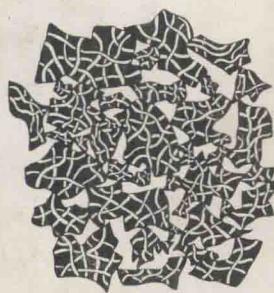
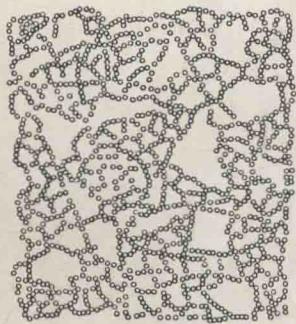
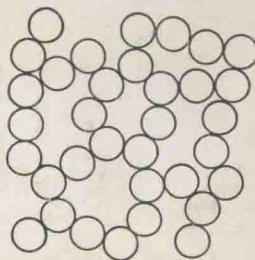
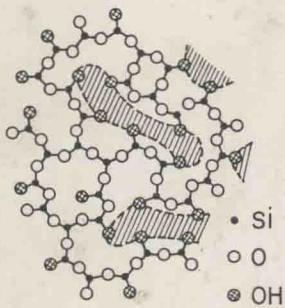


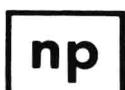
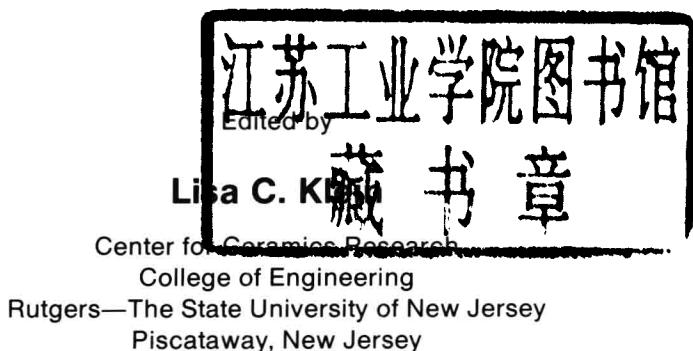
SOL-GEL TECHNOLOGY FOR THIN FILMS, FIBERS, PREFORMS, ELECTRONICS AND SPECIALTY SHAPES



Edited by
Lisa C. Klein

NOYES PUBLICATIONS

SOL-GEL TECHNOLOGY FOR THIN FILMS, FIBERS, PREFORMS, ELECTRONICS, AND SPECIALTY SHAPES



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

Copyright © 1988 by Noyes Publications

**No part of this book may be reproduced or utilized in
any form or by any means, electronic or mechanical,
including photocopying, recording or by any informa-
tion storage and retrieval system, without permission
in writing from the Publisher.**

Library of Congress Catalog Card Number: 87-34780

ISBN: 0-8155-1154-X

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

**Sol-Gel technology for thin films, fibers, preforms,
electronics, and speciality shapes.**

Bibliography: p.

Includes index.

1. Ceramic materials. 2. Glass fibers.

**3. Thin films. 4. Colloids. I. Klein, Lisa C.
TP862.S65 1988 666'.15 87-34780**

ISBN 0-8155-1154-X

**SOL-GEL TECHNOLOGY
FOR THIN FILMS, FIBERS, PREFORMS,
ELECTRONICS, AND SPECIALTY SHAPES**

MATERIALS SCIENCE AND PROCESS TECHNOLOGY SERIES

Editors

Rointan F. Bunshah, University of California, Los Angeles (*Materials Science and Technology*)

Gary E. McGuire, Microelectronics Center of North Carolina (*Electronic Materials and Processing*)

DEPOSITION TECHNOLOGIES FOR FILMS AND COATINGS; Developments and Applications: by *Rointan F. Bunshah et al*

CHEMICAL VAPOR DEPOSITION FOR MICROELECTRONICS; Principles, Technology, and Applications: by *Arthur Sherman*

SEMICONDUCTOR MATERIALS AND PROCESS TECHNOLOGY HANDBOOK; For Very Large Scale Integration (VLSI) and Ultra Large Scale Integration (ULSI): edited by *Gary E. McGuire*

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

HYBRID MICROCIRCUIT TECHNOLOGY HANDBOOK; Materials, Processes, Design, Testing and Production: by *James J. Licari and Leonard R. Enlow*

HANDBOOK OF THIN FILM DEPOSITION PROCESSES AND TECHNIQUES; Principles, Methods, Equipment and Applications: edited by *Klaus K. Schuegraf*

Related Titles

ADHESIVES TECHNOLOGY HANDBOOK: by *Arthur H. Landrock*

HANDBOOK OF THERMOSET PLASTICS: edited by *Sidney H. Goodman*

HANDBOOK OF CONTAMINATION CONTROL IN MICROELECTRONICS; Principles, Applications and Technology: edited by *Donald L. Tolliver*

*To my daughter, Martha Ann Kinsella, who
was born while the book was in progress.*

and

*To Dennis Ravaine, my scientific collabora-
tor and friend, who passed away suddenly
in 1986.*

Preface

This book covers the principles, developments, techniques, and applications of sol-gel processing. The sol-gel process is not new, however, a few commercial successes in the recent past have revived interest. The commercial successes are largely in the area of thin films. These films have been developed for optical, mechanical and electrical applications. About one-third of this book covers thin films.

The second area where there has been commercial success is fibers. These fibers whether spun or drawn may be continuous or woven. The applications realized and projected are refractories, composite reinforcement and thermal insulation. About one-third of this book covers fibers.

The third area encompasses the special applications such as preforms, micro-balloons and electronics. Discussion of the chemistry, polymerization, drying and characterization are all necessary parts of a treatment of sol-gel processing.

The anticipated product of this effort is a book that covers the background and fundamentals. Also, it evaluates the present technology and projects new directions short range and long range.

The graduate students at Rutgers University, P. Anderson, H. deLambilly, T. Gallo, T. Lombardi and J. Ryan, are thanked for their editorial assistance. Visiting scientists Jean-Yves Chane-Ching and Henry Wautier served as reviewers.

Center for Ceramics Research
Rutgers-The State University of New Jersey
Piscataway, New Jersey
December 1987

Lisa C. Klein

Contributors

Carol S. Ashley

Sandia National Laboratories
Albuquerque, New Mexico

John B. Blum

Norton Company
Northboro, Massachusetts

Jean Pierre Boilot

Groupe de Chimie du Solide
Laboratoire de Physique de la
Matiere Condensee
Ecole Polytechnique
Palaiseau, France

C. Jeffrey Brinker

Sandia National Laboratories
Albuquerque, New Mexico

Richard K. Brow

Department of Materials Science
and Engineering
The Pennsylvania State University
University Park, Pennsylvania

Lee A. Carman

Department of Materials Science
and Engineering
The Pennsylvania State University
University Park, Pennsylvania

Philippe Colombar

Groupe de Chimie du Solide
Laboratoire de Physique de la
Matiere Condensee
Ecole Polytechnique
Palaiseau, France

Helmut Dislich

Schott Glaswerke
Mainz, Federal Republic of
Germany

Raymond L. Downs

KMS Fusion, Inc.
Ann Arbor, Michigan

Matthias A. Ebner

KMS Fusion, Inc.
Ann Arbor, Michigan

Jochen Fricke

Physikalisches Institut der
Universitat Am Habland
Wurzburg, West Germany

Stephen H. Garofalini

Ceramics Department
Rutgers—The State University of
New Jersey
Piscataway, New Jersey

x Contributors

Lisa C. Klein
Ceramics Department
Rutgers—The State University of
New Jersey
Piscataway, New Jersey

William C. LaCourse
Alfred University
Alfred, New York

Wayne J. Miller
KMS Fusion, Inc.
Ann Arbor, Michigan

Shyama P. Mukherjee
IBM Corporation
Endicott, New York

George F. Neilson
Microgravity Science and
Applications Group
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Richard B. Pettit
Sandia National Laboratories
Albuquerque, New Mexico

Carlo G. Pantano
Department of Materials Science
and Engineering
The Pennsylvania State University
University Park, Pennsylvania

Eliezer M. Rabinovich
AT&T Bell Laboratories
Murray Hill, New Jersey

Scott T. Reed
Sandia National Laboratories
Albuquerque, New Mexico

Sumio Sakka
Institute for Chemical Research
Kyoto University
Uji, Kyoto-Fu, Japan

Harold G. Sowman
3M
St. Paul, Minnesota

Ian M. Thomas
Lawrence Livermore National
Laboratory
University of California
Livermore, California

Michael C. Weinberg
Microgravity Science and
Applications Group
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

Masayuki Yamane
Department of Inorganic Materials
Tokyo Institute of Technology
Tokyo, Japan

NOTICE

To the best of the Publisher's knowledge the information contained in this publication is accurate; however, the Publisher assumes no liability for errors or any consequences arising from the use of the information contained herein. Final determination of the suitability of any information, procedure, or product for use contemplated by any user, and the manner of that use, is the sole responsibility of the user.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Publisher.

The book is intended for informational purposes only. The reader is warned that caution must always be exercised when dealing with hazardous materials, and expert advice should be obtained at all times when implementation is being considered.

Contents

PART I CHEMISTRY AND PHASE TRANSFORMATIONS

1. MULTICOMPONENT GLASSES FROM THE SOL-GEL PROCESS	2
<i>Ian M. Thomas</i>	
Historical Introduction	2
Preparation	3
General	3
All-Alkoxide Method	3
Alkoxide-Salt Method	6
Other Methods	8
Properties	9
Homogeneity	9
Comparison with Conventional Glass.	10
Purity	10
Fabrication and Use.	11
General	11
Bulk Glass by Melting.	11
Bulk Glass Without Melting.	12
Commercial Products.	12
Conclusions	13
References	13
2. SIMULATION OF THE SOL-GEL PROCESS	16
<i>Stephen H. Garofalini</i>	
Introduction	16
Computational Procedure	18
Results and Discussion	23
Conclusions	26
References	26

3. PHASE TRANSFORMATION IN GELS: A COMPARISON OF THE PHASE TRANSFORMATION BEHAVIOR OF GEL-DERIVED AND ORDINARY $\text{Na}_2\text{O-SiO}_2$ GLASSES.	28
<i>Michael C. Weinberg and George F. Neilson</i>	
Introduction.	28
Metastable Liquid-Liquid Immiscibility in $\text{Na}_2\text{O-SiO}_2$ Glass	30
Immiscibility Temperatures.	30
Initial Study of Phase Separation of Gel-Derived Glass	32
Morphology of Phase Separation	32
Immiscibility Temperature	32
Compositional Effects	37
Factors Affecting Phase Separation Behavior	38
Trace Impurities	38
Water	39
Structure	41
Phase Separation Kinetics	41
Recent Studies	43
Crystallization of $\text{Na}_2\text{O-SiO}_2$ Gel and Glass	44
Summary and Conclusions	46
References	46
PART II	
COATINGS, THIN FILMS AND SURFACE TREATMENT	
4. THIN FILMS FROM THE SOL-GEL PROCESS	50
<i>Helmut Dislich</i>	
Introduction and Highlights of the Sol-Gel Process.	50
Principles of the Sol-Gel Dip Process	51
Process Technology	52
Process Advantages	52
Other Coating Techniques	54
Chemistry and Physical Principles of the Sol-Gel Dip Process	54
General Comments	54
Single Oxides	55
Mixed Oxides	57
Cermets	57
Non-Oxide Layers	58
Multi-Component Oxide Layers	58
Organic-Inorganic Layers	60
Coated Products Based on Sol-Gel Technology	63
Rear View Mirrors for Automobiles	63
Solar Reflecting Glass (IROX)	64
Anti-Reflective Coatings	67
Other Surface Coated Glasses	68
Sol-Gel Layers Under Development.	68
Antireflective Coatings	69
Contrast Enhancing Filters for Data Display Screens	69
Porous Antireflective Coatings in the UV-Range	69

Antireflective Coating of Silicon Solar Cells	70
Leaching of Multicomponent Oxide Layers	70
Spray-Coated Diffusor Layers	70
Transparent, Electric Conducting, IR-Reflecting Layers	72
Indium-Tin-Oxide Layers	72
Cadmium Stannate	73
Opto-Electronic Films	74
Magnetic Films	74
Barrier Films	74
Sulfide Films	74
Glassy Thick Films	75
Unsupported Glass Films	75
New Oxide-Based Gel Films.	75
Organic Modified Silicate Films	75
Scuff Resistant Layers	75
Solid Phase System for Radio Immuno Assay	75
Protective Coatings	76
Conclusions	76
References	76
5. ANTIREFLECTIVE FILMS FROM THE SOL-GEL PROCESS	80
<i>Richard B. Pettit, Carol S. Ashley, Scott T. Reed and</i>	
<i>C. Jeffrey Brinker</i>	
Introduction.	80
Optical Properties of Thin Films.	81
Sol-Gel Processing	84
AR Coatings.	85
Microstructure Tailoring.	87
Applications.	91
AR Coatings on Silicon Solar Cells	91
Antireflection Coatings on Glass.	94
Full Scale Process Development	98
Aging and Etching Conditions	98
Adaptation to Tubular Geometries	98
Sol-Gel AR Films on Plastics	99
Summary	102
Appendix: Optical Modeling.	103
References	109
Appendix References	109
6. OXYNITRIDE THIN FILMS FROM THE SOL-GEL PROCESS	110
<i>Carlo G. Pantano, Richard K. Brow and Lee A. Carman</i>	
Introduction.	110
Thermochemistry in the Si–O–N–H System.	111
Film Formation	116
Film Composition and Structure	118
Optical Properties	123
Electrical Properties	127

Oxidation Resistance	131
Summary	136
References	136
 PART III	
CONTINUOUS, DISCONTINUOUS AND WOVEN FIBERS	
7. FIBERS FROM THE SOL-GEL PROCESS	140
<i>Sumio Sakka</i>	
Introduction	140
Variations of Sol-Gel Fiber Preparation	141
Fibers Through Low Temperature Drawing from Metal	
Alkoxide Sols	142
Significance of Fiber Drawing at Low Temperature	142
Conditions for Gel-Fiber Drawing	144
Possibility of Fiber Drawing	144
Time Period Required for the Reaction Leading to Occurrence of Spinnability	145
Shape of Fiber Cross-Section	146
Process of Hydrolysis-Polycondensation	146
Reduced Viscosity	146
Intrinsic Viscosity	147
The Nature of Linear Polymeric Particles	150
Fibers of Compositions Other Than Silica	151
Properties of Fibers Synthesized by the Sol-Gel Process	152
Basic Properties	152
Properties of New Glasses: Alkali-Resistance of Zirconia- Containing Fibers	152
Appearance of Films	153
Mechanical Strength of Fibers	153
Fibers Formed by the Unidirectional Freezing of Gel	154
Preparation of the Fiber	155
Properties of Fibers Made by Unidirectional Freezing	158
References	159
8. ALUMINA-BORIA-SILICA CERAMIC FIBERS FROM THE SOL-GEL PROCESS	162
<i>Harold G. Sowman</i>	
Introduction	162
Processing	163
$\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ Fibers	163
The Effect of Boric Oxide Additions	164
Microstructure Development	165
Properties of $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ Fibers	173
$\text{Al}_2\text{O}_3-\text{SiO}_2$ Fibers	173
Commercial $\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ Fibers	175
Applications	177
Ceramic Fiber-Metal Composites	177

Ceramic Fiber-Polymer Composites	177
Flame Barriers	177
Ceramic-Ceramic Composites.	177
High Temperature Fabric	179
Modified Al₂O₃-B₂O₃-SiO₂ Fibers	179
Leached Al ₂ O ₃ -B ₂ O ₃ -SiO ₂ Fibers.	179
Cermet Fibers.	180
Summary.	182
References	182
9. CONTINUOUS FILAMENT FIBERS BY THE SOL-GEL PROCESS	184
<i>William C. LaCourse</i>	
Introduction.	184
Sol Structure	184
Sol Requirements for Continuous Filament Formation.	184
Initial Sol Structure	185
Summary-Sol Structure	188
Processes for Silica Fiber.	188
Mixing.	188
Prereaction.	188
Sol Aging.	189
Drawing.	190
Silica Fiber Properties	191
As Drawn Fibers	191
Consolidated Fibers	192
TiO ₂ , ZrO ₂ , and Binary Oxide Fibers	194
Closing Comments.	196
References	197
PART IV	
MONOLITHS, SHAPES AND PREFORMS	
10. MONOLITH FORMATION FROM THE SOL-GEL PROCESS	200
<i>Masayuki Yamane</i>	
Introduction.	200
Gel Preparation.	201
Types of Gels Used for Monolith Formation.	201
Gel Formation from Silicon Alkoxide	201
Composition of Precursor Solution.	201
Effect of Catalyst	203
Effect of Temperature	203
Drying.	204
Gel Properties.	205
Pore Size Distribution and Specific Surface Area.	205
Hydroxyl Groups and Residual Organic Compounds	209
Change in Structure and Properties of a Gel with Heat Treatment.	211
Differential Thermal Analysis and Thermogravimetric Analysis.	211

Change in Density and Linear Shrinkage	213
True Density	213
Bulk Density	214
Linear Shrinkage	215
IR and Raman Spectra	215
Change in Pore Size Distribution	217
Change with Linear Heating Rate	217
Change Under Isothermal Treatment	219
Heat Cycle for the Densification of an Alkoxy-Derived Monolithic Gel	221
References	222
11. THERMAL INSULATION MATERIALS FROM THE SOL-GEL PROCESS	226
<i>Jochen Fricke</i>	
Introduction	226
Thermal Transport in Evacuated Porous Superinsulations	230
Radiative Transport	230
Solid Thermal Conduction	233
Thermal Transport in Aerogel Tiles	234
General Considerations	234
Calorimetric Measurements	237
Effects of Gas Pressure	239
Thermal Transport in Granular Aerogel	241
General Aspects	241
Calorimetric Measurements	242
Effects of Gas Pressure	243
Optical Transparency	244
Conclusions and Outlook	245
References	245
12. ULTRAPURE GLASSES FROM SOL-GEL PROCESSES	247
<i>Shyama P. Mukherjee</i>	
Introduction	247
Methods of Making Ultrapure Glasses	248
Sol-Gel Processes	249
Glasses from Colloids	249
Glasses from Gels Prepared by the Hydrolytic Polycondensation of Metal Alkoxides/Metal Organics	249
Selection of Starting Metal Alkoxides	250
Synthesis of Homogeneous Gels/Gel-Monoliths	252
Drying of Gel-Monoliths/Gel-Powders	253
Removal of Residual Organics and Hydroxyl Groups	253
Approach 1	254
Approach 2	254
Conversion of Gel to Glass	255
Gel Processing in a Clean Room Facility	255
Conclusion	256

References	258
13. PARTICULATE SILICA GELS AND GLASSES FROM THE SOL-GEL PROCESS	260
<i>Eliezer M. Rabinovich</i>	
Introduction	260
Sources of Silica Powders and Particles	262
Gels from Alkali Silicates	264
Glasses from High-Surface Area Particulate Gels	266
Fumed Silica Gels	266
Dispersion	266
Gelation	266
Drying and Double Processing	268
Combined Alkoxide-Particulate Method	274
Sintering of Gel to Glass	276
Elimination of Bubble Formation on Reheating of Gel Glasses	280
General Scheme of the Process; Properties of Glasses	283
Glasses from Low Surface Area Powders	283
Doping Particulate Gel Glasses	287
Applications of Particulate Gel Glasses	290
Summary	291
References	292
 PART V	
SPECIAL APPLICATIONS	
14. ELECTRONIC CERAMICS MADE BY THE SOL-GEL PROCESS	296
<i>John B. Blum</i>	
Introduction	296
Advantages and Disadvantages	297
Potential Uses in Electronic Applications	298
Piezoelectrics	298
Sensors	299
Microelectronic Packaging	300
Magnetics	301
Ferroelectrics	301
Summary	301
References	302
15. SUPERIONIC CONDUCTORS FROM THE SOL-GEL PROCESS	303
<i>Jean Pierre Boilot and Philippe Colombar</i>	
Introduction: Fast Ion Conduction	303
New Amorphous Superionic Conductors	305
Transition Metal Oxide Gels	305
Sodium Lithium Superionic Gels and Glasses	306
Optically Clear Monolithic Gels	306
Homogeneity and Densification of Gels	309