

Topics in Applied Physics

Volume 106

Available **online** at
Springer Link.com

Topics in Applied Physics is part of the SpringerLink service. For all customers with standing orders for Topics in Applied Physics we offer the full text in electronic form via SpringerLink free of charge. Please contact your librarian who can receive a password for free access to the full articles by registration at:

springerlink.com → Orders

If you do not have a standing order you can nevertheless browse through the table of contents of the volumes and the abstracts of each article at:

springerlink.com → Browse Publications

Topics in Applied Physics

Topics in Applied Physics is a well-established series of review books, each of which presents a comprehensive survey of a selected topic within the broad area of applied physics. Edited and written by leading research scientists in the field concerned, each volume contains review contributions covering the various aspects of the topic. Together these provide an overview of the state of the art in the respective field, extending from an introduction to the subject right up to the frontiers of contemporary research.

Topics in Applied Physics is addressed to all scientists at universities and in industry who wish to obtain an overview and to keep abreast of advances in applied physics. The series also provides easy but comprehensive access to the fields for newcomers starting research.

Contributions are specially commissioned. The Managing Editors are open to any suggestions for topics coming from the community of applied physicists no matter what the field and encourage prospective editors to approach them with ideas.

Managing Editor

Dr. Claus E. Ascheron

Springer-Verlag GmbH

Tiergartenstr. 17

69121 Heidelberg

Germany

Email: claus.ascheron@springer.com

Assistant Editor

Adelheid H. Duhm

Springer-Verlag GmbH

Tiergartenstr. 17

69121 Heidelberg

Germany

Email: adelheid.duhm@springer.com

Marco Fanciulli Giovanna Scarel (Eds.)

Rare Earth Oxide Thin Films

Growth, Characterization, and Applications

With 210 Figures and 25 Tables

 Springer

Prof. Marco Fanciulli

Laboratorio Nazionale MDM CNR-INFM
Via C. Olivetti 2
20041 Agrate
Brianza (MI), Italy

Dr. Giovanna Scarel

Laboratorio Nazionale MDM CNR-INFM
Via C. Olivetti 2
20041 Agrate
Brianza (MI), Italy

Library of Congress Control Number: 2006935383

Physics and Astronomy Classification Scheme (PACS):
71.55.-i; 72.80.Sk; 73.20.At; 75.47.Lx; 77.55.+f

ISSN print edition: 0303-4216

ISSN electronic edition: 1437-0859

ISBN-10 3-540-35796-3 Springer Berlin Heidelberg New York

ISBN-13 978-3-540-35796-4 Springer Berlin Heidelberg New York

This work is subject to copyright. All rights are reserved, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilm or in any other way, and storage in data banks. Duplication of this publication or parts thereof is permitted only under the provisions of the German Copyright Law of September 9, 1965, in its current version, and permission for use must always be obtained from Springer. Violations are liable for prosecution under the German Copyright Law.

Springer is a part of Springer Science+Business Media

springer.com

© Springer-Verlag Berlin Heidelberg 2007

The use of general descriptive names, registered names, trademarks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

Typesetting: DA-TeX · Gerd Blumenstein · www.da-tex.de
Production: LE-TeX Jelonek, Schmidt & Vöckler GbR, Leipzig
Cover design: WMXDesign GmbH, Heidelberg

Printed on acid-free paper 57/3100/YL 5 4 3 2 1 0

Contents

Scientific and Technological Issues Related to Rare Earth Oxides: An Introduction

Giovanna Scarel, Axel Svane, Marco Fanciulli	1
1 Introduction	1
2 Thermodynamical Stability	2
3 Band Structure and Band Offsets	3
4 Dielectric Constant – κ	7
5 Effects of the Monotonously Changing Properties: The Ionic Radii ..	8
6 Summary	9
References	10
Index	13

Atomic Layer Deposition of Rare Earth Oxides

Jani Päiväsaari, Jaakko Niinistö, Pia Myllymäki, Chuck Dezelah IV, Charles H. Winter, Matti Putkonen, Minna Nieminen, Lauri Niinistö ..	15
1 Introduction	16
2 Principles of ALD	16
3 Binary RE-Oxide Thin Films by ALD	17
4 Oxygen-Coordinated Precursors	19
5 Carbon-Coordinated Precursors	21
6 Nitrogen-Coordinated Precursors	23
7 Multi-Component RE-Containing Oxide Thin Films	24
8 Multi-Component Oxides Containing One RE Metal	25
9 Multi-Component Oxides Containing Two REs	26
10 Concluding Remarks	27
References	28
Index	32

MOCVD Growth of Rare Earth Oxides:

The Case of the Praseodymium/Oxygen System

Raffaella Lo Nigro, Graziella Malandrino, Roberta G. Toro, Ignazio L. Fragalà	33
1 Introduction	33
2 MOCVD Precursors	35

2.1	Praseodymium β -Diketonate Precursors: Pr(hfa) ₃ •Diglyme and Pr(tmhd) ₃ Complexes	36
3	Thermal MOCVD	38
3.1	Film Growth from Pr(tmhd) ₃	38
3.2	Study of the Praseodymium Oxide Growth Process Through the Thermal MOCVD Process	40
3.3	Characterization of the Film/Substrate Interface	40
3.4	Electrical Characterization	42
3.5	Film Growth from Pr(hfa) ₃ •Diglyme	43
4	MOCVD Growth of Mixed Pr/Al Oxide Films	44
5	Summary	46
	References	47
	Index	51

Requirements of Precursors for MOCVD and ALD of Rare Earth Oxides

	Helen C. Aspinall	53
1	Introduction to Rare Earth Chemistry	53
2	Requirements for MOCVD and ALD Precursors	55
2.1	Making Rare Earth Complexes Volatile	55
2.2	Chemical Requirements of Precursors for MOCVD	63
2.3	Chemical Requirements of Precursors for ALD	65
3	Conclusions	68
	References	68
	Index	72

Models for ALD and MOCVD Growth of Rare Earth Oxides

	Simon D. Elliott	73
1	Introduction	73
2	Modelling Deposition Reactions	74
2.1	Suitability of Electronic Structure Theory	74
2.2	Atomic-Scale Models	75
2.3	Reaction Steps in ALD	76
3	Analytical Models for ALD Film Growth	79
4	Continuum Models for Gas Transport	81
5	Conclusion	83
	References	84
	Index	86

Growth of Oxides with Complex Stoichiometry by the ALD Technique, Exemplified by Growth of La_{1-x}Ca_xMnO₃

	Ola Nilsen, Martin Lie, Helmer F. Fjellvåg, Arne Kjekshus	87
1	Introduction	87
2	Conceptual Basis for ALD Deposition of Complex Stoichiometries	88
2.1	The Model System	89

2.2 Deposition of Binary Compounds 90
 2.3 Deposition of Ternary Compounds 90
 2.4 Deposition of Quaternary Compounds 94
 3 Conclusions 95
 References 96
 Index 99

Molecular Beam Epitaxy of Rare-Earth Oxides

H. Jörg Osten, Eberhard Bugiel, Malte Czernohorsky, Zeyard Elassar,
 Olaf Kirfel, Andreas Fissel 101
 1 Introduction 101
 2 Epitaxial Metal Oxides on Silicon 103
 3 Results for the Growth of Different Rare-Earth Oxides on Silicon . . 105
 3.1 Experimental 105
 3.2 Epitaxial Growth on Si(100) 106
 3.3 Epitaxial Growth on Si(111) 107
 3.4 Interface Stability 107
 4 Outlook 112
 References 113
 Index 114

**Fabrication and Characterization of Rare Earth Scandate
 Thin Films Prepared by Pulsed Laser Deposition**

Jürgen Schubert, Tassilo Heeg, Martin Wagner 115
 1 Introduction 115
 2 Pulsed Laser Deposition 117
 3 Epitaxial Films 118
 4 Amorphous Films 122
 5 Conclusions 124
 References 125
 Index 126

**Film and Interface Layer Composition of Rare Earth (Lu,
 Yb) Oxides Deposited by ALD**

Yuri Lebedinskii, Andrei Zenkevich, Giovanna Scarel, Marco Fanciulli . 127
 1 Introduction 127
 2 Experimental 128
 3 Results and Discussion 130
 3.1 Lu₂O₃ 130
 3.2 Yb₂O₃ 132
 3.3 Lu Silicate Layers on Si 133
 3.4 Ultrathin Lu₂O₃ and Yb₂O₃ Layers on Si(100) 135
 3.5 Ultrathin Lu₂O₃ on Ge(100) 139
 4 Conclusions 140
 References 141
 Index 142

Local Atomic Environment of High- κ Oxides on Silicon Probed by X-Ray Absorption Spectroscopy

Marco Malvestuto, Federico Boscherini 143

1 X-Ray Absorption Spectroscopy in the Study of Rare Earth Oxides 143

2 Case Studies: Y_2O_3 and Lu_2O_3 on Si(001) 146

3 Conclusions 150

References 150

Index 152

Local Structure, Composition and Electronic Properties of Rare Earth Oxide Thin Films Studied Using Advanced Transmission Electron Microscopy Techniques (TEM-EELS)

Sylvie Schamm, Giovanna Scarel, Marco Fanciulli 153

1 Introduction 153

2 State of the Art 154

 2.1 Thickness Measurement 155

 2.2 Lattice Images 156

 2.3 EELS Analysis 158

 2.4 Sample Preparation 161

3 The Case of Lu_2O_3/Si 162

 3.1 Conventional TEM 162

 3.2 Lattice Imaging 163

 3.3 EFTEM-EELS 164

 3.3.1 Fine Structure of Reference Samples 165

 3.3.2 Si/ Lu_2O_3 Stacks 167

4 Discussion and Conclusions 172

References 172

Index 176

Strain-Relief at Internal Dielectric Interfaces in High- k Gate Stacks with Transition Metal and Rare Earth Atom Oxide Dielectrics

Gerald Lucovsky, James C. Phillips 179

1 Introduction 179

2 Chemical Bonding Changes at Si-SiO₂ Interfaces after High-Temperature Annealing 182

 2.1 Spectroscopic Studies 182

 2.2 Kinetics of Interfacial Changes at the Interface Bonding and Defect Levels 185

 2.3 Bond Constraint Theory and the SiO_x Bonding Changes 186

 2.4 Self-Organization Transition at Si-SiO₂ Interfaces 188

3 Internal Dielectric Interfaces 190

 3.1 Fixed Charge at Internal Dielectric Interfaces 190

 3.2 BCT and Internal Dielectric Interfaces 190

3.3	Interfacial Relaxation and Phase Diagrams	191
4	Discussion	194
4.1	Defects in High- k Gate Stacks	194
4.2	EOT Scaling in Advanced Gate Stacks	196
4.3	Narrowing the Field of High- k Dielectrics	196
	References	199
	Index	202

Electrical Characterization of Rare Earth Oxides Grown by Atomic Layer Deposition

Sabina Spiga, Claudia Wiemer, Giovanna Scarel, Omar Costa, Marco Fanciulli		203
1	Introduction	203
2	Experimental Methods	206
3	Yb ₂ O ₃ Grown by ALD	208
3.1	Structural Characterization	208
3.2	Electrical Characteristics and Interface Defects	209
4	Lu ₂ O ₃ Grown by ALD	214
4.1	Structural Characterization	214
4.2	Electrical Characteristics and Interface Defects	215
5	Conclusions	218
	References	219
	Index	223

Dielectric Properties of Rare-Earth Oxides: General Trends from Theory

Pietro Delugas, Vincenzo Fiorentini, Alessio Filippetti		225
1	Introduction and Theoretical Tools	225
1.1	Linear Response Theory and Dielectric Properties	226
2	Sesquioxides	229
2.1	Lutetia, Lanthana, and the Hex–Bix Differences	230
3	Aluminates	235
3.1	Crystalline LaAlO ₃	236
3.2	Conservation of High κ in Amorphous Ln-Aluminates?	238
3.3	Dielectric Enhancement in Aluminate Alloys	241
4	Conclusions	242
	References	243
	Index	246

Charge Traps in High- k Dielectrics: Ab Initio Study of Defects in Pr-Based Materials

Jarek Dąbrowski, Andrzej Fleszar, Gunther Lippert, Grzegorz Lupina, Anil Mane, Christian Wenger		247
1	Theoretical Approach	247
2	Charge Traps	249
2.1	Trap Assisted Tunneling Centers	249

2.2	Fixed Charges	250
3	Native Point Defects	251
3.1	Native Defects in Pr_2O_3	251
3.2	Selected Native Defects in PrO_2	253
3.3	Selected Native Defects in $\text{PrO}_{1.75+\delta}$	254
3.4	Selected Native Defects in $\text{Pr}_2\text{Si}_2\text{O}_7$	255
3.5	Selected Native Defects in SiO_2	258
4	Impurities	260
4.1	Moisture	260
4.2	Silicon	261
4.3	Boron	264
4.4	Titanium	265
5	Summary and Conclusions	265
	References	266
	Index	267

Experimental Determination of the Band Offset of Rare Earth Oxides on Various Semiconductors

	Gabriele Seguini, Michele Perego, Marco Fanciulli	269
1	Introduction	269
2	Experimental Techniques for Band Offset Determination	270
2.1	Internal Photoemission	270
2.2	X-Ray Photoelectron Spectroscopy	272
3	Literature Results	274
4	Lu_2O_3 on Si, Ge and GaAs	274
4.1	Experimental	274
4.2	Results and Discussion	275
5	Conclusions	279
	References	280
	Index	282

Band Edge Electronic Structure of Transition Metal/Rare Earth Oxide Dielectrics

	Gerald Lucovsky	285
1	Introduction	285
2	Experimental Methods	287
3	Experimental Results and Discussion: TM Elemental Oxides	287
4	Experimental Results: TM/RE Complex Oxides	295
5	Experimental Results: Intrinsic Defect States	301
6	Experimental Results: Zr Silicate and Si Oxynitride Alloys	304
7	Conclusions	307
	References	310
	Index	311

Electronic Structure and Band Offset of Lanthanide Oxides

John Robertson, Ka Xiong	313
1 Introduction	313
2 Bulk Electronic Structure	315
3 Band Offsets	319
4 Explicit Calculations	324
5 Conclusions	326
References	326
Index	329

Electronic Structure of Rare Earth Oxides

Leon Petit, Axel Svane, Zdzisława Szotek, Walter M. Temmerman	331
1 Introduction	331
2 SIC-LSD Formalism	332
3 Rare Earth Dioxides	334
4 Sesquioxides	336
5 Conclusions	341
References	342
Index	343

Rare Earth Oxides in Microelectronics

Kuniyuki Kakushima, Kazuo Tsutsui, Sun-Ichiro Ohmi, Parhat Ahmet, V. Ramgopal Rao, Hiroshi Iwai	345
1 Introduction	346
2 Issues in High- κ Materials	347
3 Short Channel Effect Enhancement	348
4 Hygroscopic Properties of Rare Earth Oxide Materials	349
5 La_2O_3 Deposition	352
6 Electrical Properties of La_2O_3 MIS Capacitors	354
7 Conduction Mechanisms of La_2O_3 MISCAP	356
8 Electrical Properties of MISFET with La_2O_3 Gate Insulator	357
9 Low Noise Frequency Measurement	360
10 Interfacial Layer Suppression	361
11 Conclusions	362
References	363
Index	365

Requirements of Oxides as Gate Dielectrics for CMOS Devices

Gennadi Bersuker, Peter Zeitzoff	367
1 Introduction	367
2 General Properties of Metal Oxides	369
3 Technological Requirements for Novel Gate Dielectrics	373
References	375
Index	377

Rare Earth Oxides Grown by Molecular Beam Epitaxy for Ultimate Scaling

Athanasios Dimoulas 379

1 Introduction 379

2 Substrate Cleaning and Thin Film Preparation Methodology 381

3 Lanthanum-Based Compounds on Silicon Substrates 382

4 Ceria on Germanium and GaAs Substrates 385

5 Summary and Future Outlook 387

References 388

Index 390

The Magneto-Electric Properties of RMnO_3 Compounds

Thomas T. M. Palstra 391

1 Introduction 391

2 ABO_3 Perovskites 392

3 AMnO_3 Hexagonal Manganites 394

4 Novel Mechanisms 396

5 Conclusions 397

References 397

Index 399

Sesquioxides as Host Materials for Rare-Earth-Doped Bulk Lasers and Active Waveguides

Sebastian Bär, Hanno Scheife, Klaus Petermann, Günter Huber 401

1 Introduction 401

2 Rare-Earth-Doped Sesquioxide Lasers 403

3 Thin Film Preparation 405

 3.1 Pulsed Laser Deposition 407

 3.2 Electron Beam Evaporation 408

4 Analytical Techniques and Thin Film Characterization 409

 4.1 Atomic Force Microscopy 409

 4.2 X-Ray Diffraction Studies 411

 4.2.1 X-Ray Diffraction 411

 4.2.2 Surface X-Ray Diffraction 413

 4.3 Rutherford Backscattering 414

 4.4 Optical Spectroscopy 414

 4.4.1 Temporal Luminescence Characteristics 417

5 Waveguides 418

6 Summary 419

References 420

Index 422

Index 423