

Springer Theses

Recognizing Outstanding Ph.D. Research

Aims and Scope

The series “Springer Theses” brings together a selection of the very best Ph.D. theses from around the world and across the physical sciences. Nominated and endorsed by two recognized specialists, each published volume has been selected for its scientific excellence and the high impact of its contents for the pertinent field of research. For greater accessibility to non-specialists, the published versions include an extended introduction, as well as a foreword by the student’s supervisor explaining the special relevance of the work for the field. As a whole, the series will provide a valuable resource both for newcomers to the research fields described, and for other scientists seeking detailed background information on special questions. Finally, it provides an accredited documentation of the valuable contributions made by today’s younger generation of scientists.

Theses are accepted into the series by invited nomination only and must fulfill all of the following criteria

- They must be written in good English.
- The topic should fall within the confines of Chemistry, Physics, Earth Sciences, Engineering and related interdisciplinary fields such as Materials, Nanoscience, Chemical Engineering, Complex Systems and Biophysics.
- The work reported in the thesis must represent a significant scientific advance.
- If the thesis includes previously published material, permission to reproduce this must be gained from the respective copyright holder.
- They must have been examined and passed during the 12 months prior to nomination.
- Each thesis should include a foreword by the supervisor outlining the significance of its content.
- The theses should have a clearly defined structure including an introduction accessible to scientists not expert in that particular field.

More information about this series at <http://www.springer.com/series/8790>

Chuan Cheng

Electro-Chemo-Mechanics of Anodic Porous Alumina Nano-Honeycombs: Self-Ordered Growth and Actuation

Doctoral Thesis accepted by
The University of Hong Kong, China

 Springer

Author

Dr. Chuan Cheng
The University of Hong Kong
Hong Kong
China

Supervisor

Prof. Alfonso H.W. Ngan
The University of Hong Kong
Hong Kong
China

ISSN 2190-5053

Springer Theses

ISBN 978-3-662-47267-5

DOI 10.1007/978-3-662-47268-2

ISSN 2190-5061 (electronic)

ISBN 978-3-662-47268-2 (eBook)

Library of Congress Control Number: 2015939669

Springer Heidelberg New York Dordrecht London

© Springer-Verlag Berlin Heidelberg 2015

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, 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.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

Springer-Verlag GmbH Berlin Heidelberg is part of Springer Science+Business Media
(www.springer.com)

Parts of this thesis have been published in the following articles:

Journal Papers:

- Cheng C, Ngan AHW (2013) Growth sustainability of nanopore channels in anodic aluminum oxide guided with prepatterns. *J Phys Chem C* 117:12183–12190 (Reproduced with Permission)
- Cheng C, Ngan AHW (2013) Charge-induced reversible bending in nanoporous alumina-aluminum composite. *Appl Phys Lett* 102:213119-1-213119-4 (Reproduced with Permission)
- Cheng C, Ngan AHW (2013) Fast fabrication of self-ordered anodic porous alumina on oriented aluminum grains by high acid concentration and high temperature anodization. *Nanotechnology* 24:215602-1-215602-10 (Reproduced with Permission)
- Cheng C, Ng KY, Aluru NR, Ngan AHW (2013) Simulation and experiment of substrate aluminum grain orientation dependent self-ordering in anodic porous alumina. *J Appl Phys* 113:204903-1-204903-9 (Reproduced with Permission)
- Cheng C, Ngan AHW (2013) Chemo-mechanical softening during in situ nanoindentation of anodic porous alumina with anodization processing. *J Appl Phys* 113:184903-1-184903-8 (Reproduced with Permission)
- Cheng C, Ng KY, Ngan AHW (2011) Quantitative characterization of acid concentration and temperature dependent self-ordering conditions of anodic porous alumina. *AIP Adv* 1: 042113-1-042113-11 (Open Access)
- Cheng C, Ngan AHW (2011) Modelling and simulation of self-ordering in anodic porous alumina. *Electrochim Acta* 56:9998-10008 (Reproduced with Permission)

Conferences (*invited):

- *Cheng C, Ngan AHW (2013) Electrochemo-mechanics of alumina nanohoneycombs: self-ordered growth and actuation. Gordon Research Conference: Nano-Mechanical Interfaces, Hong Kong University of Science and Technology, Hong Kong, China, August 04–09.
- *Cheng C, Ngan AHW (2013) Electrochemo-mechanics of alumina nanohoneycombs: ordering and actuation. 4th International Conference from Nanoparticles & Nanomaterials to Nanodevices & Nanosystems, Corfu Island, Greece, June 16–20.
- Cheng C, Ngan AHW (2013) Self-ordered anodic porous alumina formed on oriented Al grains. Poster presentation. Materials Research Society (MRS) 2013 Spring Meeting and Exhibit, San Francisco, California, USA, April 01–05.
- *Ngan, AHW, Ng, KY, Cheng, C (2012) Alumina nanohoneycombs with controlled spatial ordering of pore channels. Keynote Presentation. 2012 International Conference for Leading and Young Materials Scientists (IC-LYMS 2012), Zhuhai, China, December 16–20.
- *Ng, KY, Cheng, C, Ngan, AHW (2012) Alumina nanohoneycombs with controlled spatial ordering of pore channels—fabrication, theory and mechanical properties. Keynote Lecture, 2012 International Conference on Manufacturing Engineering and Automation (ICMEA 2012), Guangzhou, China, November 16–18.

- *Ngan, AHW, Ng, KY, Cheng, C (2011) Anodized porous alumina with controlled pore-channel ordering – fabrication, theory and mechanical properties. One of the Three Special Lectures. 6th International Conference on Advanced Materials Development and Performance, Tokushima, Japan, July 15–18.
- *Ngan, AHW, Ng, KY, Cheng, C (2010) Mechanics of nanohoneycombs. Gordon Research Conference on Thin Film and Small-scale Mechanical Behaviour, Colby College, Waterville, Maine, USA, July 25–30.

Supervisor's Foreword

This book summarizes Dr. Chuan Cheng's work during his Ph.D. study at the University of Hong Kong, from September 1, 2009 to August 31, 2013. By using both theoretical and experimental approaches, Dr. Cheng studied the self-similar growth of anodic aluminium oxide which can be made to form a characteristic nano-honeycomb structure under a small window of processing conditions. Despite the fact that this phenomenon has been known for a few decades, and that such nano-honeycomb structures are nowadays routinely employed as the template materials for making other nanomaterials for a wide range of applications, no one has been able to predict theoretically the conditions under which the self-ordered growth happens, or the detailed mechanisms involved. Dr. Cheng's work is an important step in this direction. In this book, you will see that he developed an electrochemical model, wrote computer codes for its implementation, and was able to predict the self-similar growth of the nano-honeycomb structure within a certain window of processing parameters. Furthermore, he conducted key experiments to verify certain characteristics predicted from his model. In the second part of his work, he also discovered a novel actuation response of such nano-honeycomb structures on electrical charging.

I enjoyed supervising Dr. Cheng toward his doctorate, and I hope that you will enjoy reading his work.

Hong Kong
March 2015

Prof. Alfonso H.W. Ngan

Abstract

Self-ordered anodic porous alumina with a nano-honeycomb structure has recently been extensively used as templates for the synthesis of various nanomaterials for diverse applications. However, due to insufficient knowledge on the combined electro-chemo-mechanical processes, the formation mechanism of self-ordering has been under debate for decades without clear conclusions. Also, fast fabrication of highly self-ordered and mechanically stable anodic porous alumina is still a challenge. Furthermore, the actuation behavior of anodic porous alumina on external mechanical and electrical triggering in an electrochemical cell has not been exploited.

In this work, first, we investigated the self-ordering mechanism by establishing a kinetics model involving the Laplacian electric potential distribution and a continuity equation for current density within the oxide body. Current densities governed by the Cabrera-Mott equation are formed by ion migration within the oxide as well as across the interfaces. The pore channel growth, due to electric-field-assisted reactions, is governed by Faraday's law. Real-time evolution of pre-patterned pore channel growth was simulated in two-dimensional cases by finite element method. The simulations revealed a parameter domain within which pre-patterned pore channels will continue to grow in a stable manner during the subsequent anodization if the pre-patterns are commensurate with the self-ordered configurations, or these are driven into stable if the pre-patterns do not initially match the self-ordered configurations. This was verified in experimentally observed pore channel growth under the guidance of pre-patterns made by focused-ion-beam milling. Furthermore, the simulations revealed that ionization reaction on (001) oriented Al grain is relatively easier than that on (101) grain, which results in stable and unstable pore channel growth on (001) and (101) Al grains, respectively, both of which were observed from the simulations and experiments.

Second, a scheme on quantitative evaluation of self-ordering qualities in anodic porous alumina has been developed, based on which we systematically searched the optimum self-ordering conditions, by varying the key anodization factors, including substrate grain orientation, electrolyte concentration, temperature, voltage, and time. A high acid concentration and high temperature anodization method was

found. Compared with conventional methods, the present method can realize fast formation of highly self-ordered, and mechanically stable anodic porous alumina under a continuous range of anodization voltage with tunable interpore distances.

Third, reversible bending was found in anodic porous alumina-Al composites upon cyclic electric actuation, as directly observed by an optical microscope and detected by in situ nanoindentation. The bending is thought to be the result of charge-induced surface stresses in the nanoporous alumina. The results suggest a new type of composite materials for applications as micro-scale actuators to transform electrical energy into mechanical energy. Furthermore, the composite exhibits a significant softening during in situ nanoindentation when the estimated maximum stress underneath the indenter is exerted on the metal/oxide interface. Softening was further verified by in situ microindentation. Electron microscopy examination indicated that softening is due to a combination of high compression stress and electric field acting near the interface, which enhance ionization reaction and cause the interface to move faster into the substrate.

Acknowledgments

This thesis is based on the work carried out in the Materials and Nanotechnology Laboratory at the Department of Mechanical Engineering at The University of Hong Kong from September 1, 2009 to August 31, 2013.

This thesis could not be completed without the insightful, passionate, effective, and consistent guidance of my Ph.D. supervisor Professor A.H.W. Ngan. I want to thank him for selecting me as one of his students. This changed my whole life and provided me with the precious opportunity to get closer to my childhood dream of being a scientist. During the past 4 years, we maintained an efficient and comprehensive mode of exchanging research ideas, facing and solving research problems together. Many of the research bottlenecks could not be overcome without his keen scientific insight and fruitful guidance. His diligence, passion, ethics, and high efficiency on research have set up a typical example for me of what a real scientist should be. His ideas have reshaped my mind and the way of doing research.

Next I thank both Prof. N.R. Aluru and Prof. A.H.W. Ngan for giving me the opportunity to be a visiting scholar at the University of Illinois at Urbana-Champaign for a half-year exchange during my Ph.D. stage. This provided me a chance to have a glimpse of the innovative research in the US, and also a chance to improve my oral English. Also, I would like to thank Dr. X. Jin for giving me plenty of help during my study while living in the US.

I thank Dr. K.Y. Ng for his design of the electrochemical cell described in Sect. 4.2.2, and his EDX experimental data shown in Fig. 5.5, for verification of the present modeling and simulation results. I also thank Prof. B.J. Duggan, Dr. Y. Lin, Dr. M. Huang, and Dr. B. Tang for the valuable questions and suggestions during my group presentations.

Furthermore, I thank Mr. K.K. Wong and T.K. Liu in our laboratory for providing me all the necessary experimental support. I also thank F. Chan, S.L. Wong, and W.S. Lee at the Electron Microscope Unit of HKU, for their assistance and patience in teaching me to use the facilities. I also thank Mr. W.K. Kwan for his assistance in running my calculation program on the HPCPOWER 64-bit System in the Computer Center of HKU.

Moreover, I thank my friend Dr. K.W. Siu for the discussion of research during our spare times. I thank Ms. S. Wang for sharing with me the experiences of performing anodization experiments. I also thank other lab mates, Dr. Y. Chan, Ms. S.Y. Ng, Ms. R. Gu, Mr. Z. Zhou, Ms. X.X. Chen, and Dr. K.S. Ng for the interesting discussions on research.

Finally, I thank my parents. During more than 20 years of continuous education in the campus, they have tolerated so much for me on financial and emotional issues which they never mentioned. It is their love that supports me to be here and to go on for the future. I also thank my wife for her complete understanding during the 4 years of separation.

Contents

1	Research Background and Motivation	1
1.1	General Concept of Anodic Porous Alumina	1
1.2	Various Applications of Anodic Porous Alumina	2
1.2.1	Applications in Photonic Crystals	2
1.2.2	Applications in Energy Storage and Conversion	3
1.2.3	Applications in Bio-devices	4
1.2.4	Applications in Electronic/Magnetic Devices	5
1.3	Formation Mechanisms of Anodic Porous Alumina	6
1.4	Fabrication Methods for Self-ordered Anodic Porous Alumina	10
1.4.1	Mild Anodization and Hard Anodization	10
1.4.2	Anodization with Prepatterns on Aluminum Substrate	11
1.4.3	Anodic Porous Alumina Formed on Aluminum Grains with Different Crystallographic Orientations	12
1.4.4	Other Anodization Methods	13
1.5	Objectives and Flow of the Present Research	13
	References	15
Part I Modelling, Numerical Simulation, and Experimental Verification of Self-ordering in Anodic Porous Alumina		
2	Establishment of a Kinetics Model	23
2.1	Introduction	23
2.2	Electric Potential Distribution Within Anodic Porous Alumina	23

2.3	Ion Migration	27
2.3.1	Aluminum Ion Migration	27
2.3.2	Oxygen Ion Migration	30
2.3.3	Relationship Between Aluminum Ion Current Density and Oxygen Ion Current Density Within the Oxide Body	32
2.4	Interface Movement Equations	33
2.5	Summary	34
	References.	34
3	Numerical Simulation Based on the Established Kinetics Model	37
3.1	Introduction	37
3.2	Numerical Realization of the Kinetics Model	37
3.2.1	Simulation Procedures	37
3.2.2	Simulation Parameters	39
3.3	Simulation Results and Discussion	42
3.3.1	Electric Field-Driven Pore Growth in Anodic Porous Alumina	43
3.3.2	Electric Field-Driven Self-ordering in Anodic Porous Alumina	48
3.4	Summary	58
	References.	59
4	Experimental Verification I: Growth Sustainability of Nanopore Channels Guided with Pre-patterns	61
4.1	Introduction	61
4.2	Experimental Methods.	62
4.2.1	Pretreatment of Aluminum Foils	62
4.2.2	Anodization Experimental Setup	62
4.2.3	Pre-patterning of Aluminum Surface by Focused Ion Beam Milling	63
4.2.4	Microscopic Characterization	63
4.3	Results and Discussion	63
4.4	Summary	72
	References.	72
5	Experimental Verification II: Substrate Grain Orientation-Dependent Self-ordering	75
5.1	Introduction	75
5.2	Experiments of Substrate Grain Orientation-Dependent Self-ordering	76
5.3	Simulation of Substrate Grain Orientation-Dependent Self-ordering	78

5.4	Discussion	82
5.4.1	Physical Meaning and Effects of β	82
5.4.2	Experimental Verification	84
5.5	Summary	86
	References.	86

Part II Fabrication of Highly Self-ordered Anodic Porous Alumina

6	Quantitative Evaluation of Self-ordering in Anodic Porous Alumina	91
6.1	Introduction	91
6.2	Quantitative Evaluation Methods for Porous Patterns in Anodic Porous Alumina.	92
6.2.1	Radial Distribution Function (RDF).	92
6.2.2	Angle Distribution Function (ADF).	92
6.2.3	Angular Orientation Distribution (AOD)	93
6.3	Experimental Method	95
6.4	Effects of the Quantitative Evaluation Methods.	97
6.5	Summary	104
	References.	104
7	Fast Fabrication of Self-ordered Anodic Porous Alumina on Oriented Aluminum Grains	105
7.1	Introduction	105
7.2	Experimental Methods.	106
7.2.1	Anodization of Aluminum	106
7.2.2	Microscopic Characterization	106
7.2.3	Quantitative Evaluation of Self-ordering in Porous Patterns.	108
7.2.4	Statistical Evaluation of Interpore Distance.	108
7.3	Results and Discussion	109
7.3.1	Substrate Grain Orientation-Dependent Self-ordering of Porous Patterns	109
7.3.2	Acid Concentration-Dependent Self-ordering of Porous Patterns	109
7.3.3	Temperature-Dependent Self-ordering of Porous Patterns.	111
7.3.4	Voltage-Dependent Self-ordering of Porous Patterns Under HHA and MA Conditions	115
7.3.5	Time-Dependent Self-ordering of Porous Patterns	121
7.4	Summary	124
	References.	125

Part III Electro-Chemo-Mechanical Actuations of Anodic Porous Alumina

8	Charge-Induced Reversible Bending in Anodic Porous Alumina–Aluminum Composites	129
8.1	Introduction	129
8.2	Direct Observation of the Reversible Bending by Optical Microscope.	130
8.3	Detection of the Reversible Bending by In Situ Nanoindentation	133
8.4	Discussion of the Reversible Bending	137
8.5	Summary	140
	References.	140
9	Chemomechanical Softening During In Situ Nanoindentation of Anodic Porous Alumina with Anodization Processing	143
9.1	Introduction	143
9.2	Experimental Method	144
	9.2.1 Electrochemical Cell Setup.	144
	9.2.2 In Situ and Ex Situ Nanoindentation	145
	9.2.3 Drift Correction Method for Nanoindentation	145
	9.2.4 In Situ and Ex Situ Microindentation	147
	9.2.5 Electron Microscopic Characterization	148
9.3	Softening During In Situ Nanoindentation	148
9.4	Possible Explanations of the In Situ Softening	153
	9.4.1 Electric-Field Assisted Softening of the Oxide	153
	9.4.2 Enhancement of Electrochemical Reactions at the Metal/Oxide Interface.	154
	9.4.3 Enhancement of Dislocation Activities in Aluminum Substrate	154
9.5	TEM Examination of Deformation of Oxide and Aluminum Substrate	155
9.6	Enhancement of Electrochemical Reactions at the Metal/Oxide Interface by High Electric-Field and Stresses	157
9.7	Summary	159
	References.	160

- 10 Conclusions and Future Work.** 161
 - 10.1 Conclusions 161
 - 10.2 Future Work 164
 - 10.2.1 Modeling and Numerical Simulation 164
 - 10.2.2 Fabrication. 165
 - 10.2.3 Actuation. 165
 - References. 166

- Appendix I: Calculation Program for Pore Channel Growth
in Anodic Porous Alumina** 167

- Appendix II: Calculation Program for Evaluation
of Self-ordering in Anodic Porous Alumina** 229