NANOCOMPOSITE THIN FILMS AND COATINGS

Processing, Properties and Performance

editors

Sam Zhang

Nanyang Technological University, Singapore

Nasar Ali

University of Aveiro, Portugal

Imperial College Press

Published by

Imperial College Press
57 Shelton Street
Covent Garden
London WC2H 9HE

Distributed by

World Scientific Publishing Co. Pte. Ltd.
5 Toh Tuck Link, Singapore 596224
USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601
UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Cover photo: HRTEM image (by Y. T. Pei) of magnetron sputtered nc-TiC/a-C
(by X. L. Bui)**

NANOCOMPOSITE THIN FILMS AND COATINGS

Copyright © 2007 by Imperial College Press

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN-13 978-1-86094-784-1
ISBN-10 1-86094-784-0

Typeset by Stallion Press
Email: enquiries@stallionpress.com

Printed in Singapore.

CONTENTS

Chapter 1

Magnetron Sputtered Hard and Yet Tough Nanocomposite Coatings with Case Studies: Nanocrystalline TiN Embedded in Amorphous SiN_x 1

Sam Zhang, Deen Sun and Xuan Lam Bui

1. Introduction	1
2. Deposition	3
2.1. Design of Microstructure	3
2.2. Synthesis of Thin Films	7
3. Characterization	11
3.1. Composition	11
3.2. Topography	13
3.3. Microstructure	15
3.4. Mechanical Properties	17
3.5. Oxidation Resistance	24
4. Case Studies: Silicon Nitride Nanocomposite Coating	24
4.1. Nanocrystalline TiN Embedded in Amorphous SiN _x or nc-TiN/a-SiN _x	24
4.2. Ni-Toughened nc-TiN/a-SiN _x	67
References	104

Chapter 2

Magnetron Sputtered Hard and Yet Tough Nanocomposite Coatings with Case Studies: Nanocrystalline TiC Embedded in Amorphous Carbon 111

Sam Zhang, Xuan Lam Bui and Deen Sun

1. Al-doped Amorphous Carbon: a-C(Al)	111
1.1. Composition and Microstructure	112
1.2. Mechanical Properties	117
2. Nanocrystalline TiC Embedded in Amorphous Carbon: nc-TiC/a-C	120
2.1. Composition	120

2.2. Topography	122
2.3. Microstructure	124
2.4. Mechanical Properties	130
2.5. Summary	134
3. Al-Toughened nc-TiC/a-C	134
3.1. Composition	135
3.2. Microstructure	135
3.3. Mechanical Properties	138
3.4. Thermal Stability and Oxidation Resistance	150
3.5. Application in Piston Ring	156
3.6. Summary	161
References	164

Chapter 3

Properties of Chemical Vapor Deposited Nanocrystalline Diamond and Nanodiamond/Amorphous Carbon Composite Films 167

S. C. Tjong

1. Introduction	167
2. Chemical Vapor Deposition	170
3. NCD Film Formation from Hydrogen-Deficient Plasma	176
4. NCD Films Formation from Hydrogen-Rich Plasma	183
5. Nanocomposite Film	186
6. Mechanical Behavior of NCD Films	189
7. Field Emission Characteristics	193
8. Conclusions	201
References	202

Chapter 4

Synthesis, Characterization and Applications of Nanocrystalline Diamond Films 207

Zhenqing Xu and Ashok Kumar

1. Synthesis of Diamond	207
1.1. History of Diamond	207
1.2. Structure of Diamond	208
1.3. Properties of Diamond	209
1.4. Chemical Vapor Deposition (CVD)	210
1.5. Growth Mechanisms of Microcrystalline Diamond (MCD) Films	215
1.6. Growth Mechanisms of Nanocrystalline Diamond (NCD) Films	217
2. Characterization of Nanocrystalline Diamond Films	220
2.1. Scanning Electron Microscopy (SEM)	220
2.2. Transmission Electron Microscopy (TEM)	224
2.3. Raman Spectroscopy	227

2.4. Near Edge X-Ray Absorption Fine Structure (NEXAFS)	231
2.5. X-Ray Diffraction (XRD)	234
2.6. Characterization of Mechanical Properties of NCD	234
2.7. Electron Energy Loss Spectroscopy (EELS)	238
2.8. Characterization of Electrical Properties of Doped NCD Films	239
3. Applications of NCD	244
3.1. MEMS/NEMS Applications of NCD Films	244
3.2. Electrochemistry Applications of NCD Films	251
3.3. Biomedical Applications of NCD Films	260
3.4. Field Emission Devices	266
3.5. Other Applications of NCD Films	271
4. Conclusions	273
References	274

Chapter 5

Properties of Hard Nanocomposite Thin Films 281

J. Musil

1. Introduction	281
2. Present State of Knowledge	281
3. Enhanced Hardness	282
3.1. Origin of Enhanced Hardness	282
3.2. Formation of Nanocomposite Films	283
3.3. Microstructure of Films Produced in Transition Regions	283
3.4. Microstructure of Nanocomposites with Enhanced Hardness	289
3.5. New Advanced Materials Composed of Nanocolumns	290
4. Mechanical Properties of Nanocomposite Coatings	291
5. High Temperature Behavior of Hard Nanocomposites	293
5.1. Thermal Stability of Film Properties	293
5.2. $\text{Si}_3\text{N}_4/\text{MeN}_x$ Composites with High (≥ 50 vol.%) of $\alpha\text{-Si}_3\text{N}_4$ Phase	294
5.3. Thermal Stability of Amorphous Me-Si-N Nanocomposites	299
5.4. Crystallization of Amorphous Zr-Si-N Films During Post-Deposition Thermal Annealing	299
5.5. Oxidation of Amorphous Me-Si-N Films in Flowing Air	306
5.6. Summary of Main Issues	308
6. Toughness of Thin Nanocomposite Coatings	310
6.1. Toughening Mechanisms	310
6.2. Fracture Toughness of Bulk Materials and Thin Films	311
6.3. Films and Methods Used for Characterization of Thin Film Toughness	313
6.4. Formation of Cracks	313
6.5. Assessment of Toughness of Thin Films	317
6.6. Summary of Main Issues	321

7. Future Trends	322
References	323

Chapter 6

Nanostructured, Multifunctional Tribological Coatings 329

*John J. Moore, In-Wook Park, Jianliang Lin, Brajendra Mishra
and Kwang Ho Kim*

1. Introduction	329
2. Classification of Nanostructured, Multifunctional Tribological Coatings	330
2.1. Nanoscale Multilayer Coatings	330
2.2. Nanocomposite Coatings	332
2.3. Functionally Graded Coatings	332
3. Background of Nanostructured Superhard Coatings	337
3.1. Nanoscale Multilayer Coatings	339
3.2. Single Layer Nanocomposite Coatings	341
4. New Directions for Nanostructured Supertough Coatings	342
4.1. Functionally Graded Multilayer Coatings	343
4.2. Functionally Graded Nanocomposite Coatings	345
5. Other Possible Properties of Nanostructured Coatings	346
6. New Processes for Industrial Applications of Multifunctional Tribological Coatings	347
6.1. Hybrid Coating System of Cathodic Arc Ion Evaporation (CAE) and Magnetron Sputtering (MS)	347
6.2. Pulsed Closed-Field Magnetron Sputtering (P-CFUBMS)	348
6.3. High-Power Pulsed DC Magnetron Sputtering (HPPMS)	353
7. Preparation–Microstructure–Properties of Nanostructured Coatings	354
7.1. Hybrid Coating System of Ti–Al–Si–N Coatings	354
7.2. Unbalanced Magnetron Sputtering of Ti–Si–B–C–N Coatings	357
7.3. Pulsed Closed-Field Magnetron Sputtering of Cr–Al–N Coatings	363
8. Concluding Remarks	375
References	376

Chapter 7

Nanocomposite Thin Films for Solar Energy Conversion 381

Yongbai Yin

1. Introduction	381
2. Solar Thermal Energy Conversion Nanocomposite Thin Films	381
2.1. Solar Thermal Energy Conversion Thin Films	381
2.2. Theories of Nanocomposite and Nanoparticles in Solar Thermal Energy Conversion	384

2.3. Complications in Nanocomposite Thin Film Materials in Solar Thermal Selective Surfaces: The Effects of Particle Size, Shape, and Orientation	390
3. Nanocomposite Thin Films in Solar Electrical Energy	
Conversion	395
3.1. Photovoltaic Solar Electricity Generation	395
3.2. Nanocomposite Materials in Thin Film Solar Cells	398
3.3. Dye-Sensitized Solar Cells	407
3.4. Hot-Carrier Junction Nanocomposite Solar Cells	410
4. Summary	414
References	414

Chapter 8

Application of Silicon Nanocrystal in Non-Volatile Memory Devices 419

T. P. Chen

1. Introduction	419
2. Conventional Floating Gate Non-Volatile Memory Devices	420
3. Non-Volatile Memory Devices Based on Si Nanocrystal	424
3.1. Device Structure	424
3.2. Operation Mechanisms	425
4. Synthesis and Characterization of Si Nanocrystal	429
4.1. Synthesis of Si Nanocrystal	429
4.2. Properties of Si Nanocrystal	433
5. Memory Behaviors and Performance of Si Nanocrystal Memory Devices	443
5.1. Memory Characteristics	443
5.2. Effects of Tunnel Oxide Thickness and Programming Mechanism	449
6. Single-Electron Memory Effect	462
7. Summary	466
References	467

Chapter 9

Nanocrystalline Silicon Films for Thin Film Transistor and Optoelectronic Applications 473

Youngjin Choi, Yong Qing Fu and Andrew J. Flewitt

1. Introduction	473
2. Deposition Techniques and Growth Models	474
2.1. Deposition Techniques	474
2.2. Growth Models	479
3. Characterization and Properties of nc-Si Films	482
3.1. Electrical Properties	482
3.2. Physical Properties	484

3.3. Stress Issues in Nanocrystalline Si Films	491
4. Device Applications	495
4.1. Thin Film Transistors (TFTs)	495
4.2. Solar Cells	499
4.3. Light Emitting Diodes	504
5. Conclusions	506
References	506

Chapter 10

Amorphous and Nanocomposite Diamond-Like Carbon Coatings for Biomedical Applications 513

T. I. T. Okpalugo, N. Ali, A. A. Ogwu, Y. Kousar and W. Ahmed

1. Introduction	513
2. Amorphous and Nanocomposite Diamond-Like Carbon Coatings	515
2.1. Electronic Structure	515
2.2. Plasma-Based Deposition Methods	517
2.3. Characterization	522
2.4. Doping DLC	528
2.5. Thermal Annealing	530
2.6. Biological Properties and Biocompatibility	532
2.7. Biomedical Applications	536
3. Surface Energy of Diamond-Like Carbons	538
4. Electrical Conductivity and Conduction Mechanisms	542
5. Work Function / Contact Potential Difference	545
6. Protein Adsorption on Biomaterials	549
6.1. Non-Adhesive Proteins	549
6.2. Adhesive Proteins	549
6.3. Non-Adhesive / Adhesive Protein Ratios	549
7. Endothelial Cell Interactions with Diamond-Like Surfaces	550
7.1. Silicon-Doped Diamond-Like Carbon Nanocomposite Films	552
7.2. Chromium-Doped Diamond-Like Carbon Nanocomposite Films	556
8. Summary	561
References	561

Chapter 11

Nanocoatings for Orthopaedic and Dental Application 573

Wei qi Yan

1. Introduction	573
1.1. Clinical Background	573
1.2. Biomimetic Nanoscale Biomaterials	574

2. Properties of Bone Implants	575
2.1. Concept of Biocompatibility	575
2.2. Classification of Biomaterial Implants	576
2.3. Osteogenesis Around Bone Implants	577
2.4. Materials for Orthopaedic and Dental Use	578
3. Bone Structure and Formation	581
3.1. Bone and Cells	582
3.2. Bone Formation	584
3.3. Bone Properties	585
3.4. Bone Remodeling	587
4. Bone Healing Around Implants	588
5. Implant Surface Modifications and Coatings	592
5.1. Bioactive Material Coatings	592
5.2. Hydroxyapatite-Coated Implants	593
5.3. Biomimetic Coatings on Titanium-Based Implants	595
5.4. Hybrid Coatings with Nanomaterials	598
6. Conclusion and Future Work	599
References	601
Index	607