

Nanostructured Materials and Nanotechnology VI

Ceramic Engineering and Science Proceedings
Volume 33, Issue 7, 2012

Edited by
Sanjay Mathur
Suprakas Sinha Ray

Volume Editors
Michael Halbig
Sanjay Mathur

 **WILEY**

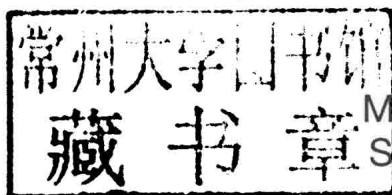
The
American
Ceramic
Society



Nanostructured Materials and Nanotechnology VI

*A Collection of Papers Presented at the
36th International Conference on Advanced
Ceramics and Composites
January 22–27, 2012
Daytona Beach, Florida*

Edited by
Sanjay Mathur
Suprakas Sinha Ray



Volume Editors
Michael Halbig
Sanjay Mathur



 **WILEY**

A John Wiley & Sons, Inc., Publication

Copyright © 2013 by The American Ceramic Society. All rights reserved.

Published by John Wiley & Sons, Inc., Hoboken, New Jersey.
Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at <http://www.wiley.com/go/permission>.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

Library of Congress Cataloging-in-Publication Data is available.

ISBN: 978-1-118-20597-6
ISSN: 0196-6219

Printed in the United States of America.

10 9 8 7 6 5 4 3 2 1

Nanostructured Materials and Nanotechnology VI

Preface

The 6th International Symposium on Nanostructured Materials and Nanotechnology was held during the 36th International Conference and Exposition on Advanced Ceramics and Composites, in Daytona Beach, Florida during January 22-27, 2012. This symposium provided, for the sixth consecutive year, an international forum for scientists, engineers, and technologists to discuss new developments in the field of nanotechnology. The symposium covered a broad perspective including synthesis, processing, modeling and structure-property correlations in nanomaterials and nanocomposites. Over 60 contributions (invited talks, oral presentations, and posters) were presented by participants from universities, research institutions, and industry, which offered interdisciplinary discussions indicating strong scientific and technological interest in the field of nanostructured systems. This issue contains 14 peer-reviewed papers cover various aspects and the latest developments related to processing of nanoscaled materials.

The editor wish to extend their gratitude and appreciation to all the authors for their cooperation and contributions, to all the participants and session chairs for their time and efforts, and to all the reviewers for their valuable comments and suggestions. Financial support from the Engineering Ceramic Division of The American Ceramic Society (ACerS) is gratefully acknowledged. The invaluable assistance of the ACerS staff of the meetings and publication departments, instrumental in the success of the symposium, is gratefully acknowledged,

We believe that this issue will serve as a useful reference for the researchers and technologists interested in science and technology of nanostructured materials and devices.

SANJAY MATHUR
University of Cologne
Cologne, Germany

SUPRAKAS SINHA RAY
National Centre for Nano Structured Materials
CSIR, Pretoria, South Africa

Introduction

This issue of the Ceramic Engineering and Science Proceedings (CESP) is one of nine issues that has been published based on content presented during the 36th International Conference on Advanced Ceramics and Composites (ICACC), held January 22–27, 2012 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society's (ACerS) Engineering Ceramics Division (ECD) since 1977.

The 36th ICACC hosted more than 1,000 attendees from 38 countries and had over 780 presentations. The topics ranged from ceramic nanomaterials to structural reliability of ceramic components which demonstrated the linkage between materials science developments at the atomic level and macro level structural applications. Papers addressed material, model, and component development and investigated the interrelations between the processing, properties, and microstructure of ceramic materials.

The conference was organized into the following symposia and focused sessions:

| | |
|-------------|--|
| Symposium 1 | Mechanical Behavior and Performance of Ceramics and Composites |
| Symposium 2 | Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications |
| Symposium 3 | 9th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology |
| Symposium 4 | Armor Ceramics |
| Symposium 5 | Next Generation Bioceramics |

| | |
|-------------------|---|
| Symposium 6 | International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution |
| Symposium 7 | 6th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications |
| Symposium 8 | 6th International Symposium on Advanced Processing & Manufacturing Technologies (APMT) for Structural & Multifunctional Materials and Systems |
| Symposium 9 | Porous Ceramics: Novel Developments and Applications |
| Symposium 10 | Thermal Management Materials and Technologies |
| Symposium 11 | Nanomaterials for Sensing Applications: From Fundamentals to Device Integration |
| Symposium 12 | Materials for Extreme Environments: Ultrahigh Temperature Ceramics (UHTCs) and Nanolaminated Ternary Carbides and Nitrides (MAX Phases) |
| Symposium 13 | Advanced Ceramics and Composites for Nuclear Applications |
| Symposium 14 | Advanced Materials and Technologies for Rechargeable Batteries |
| Focused Session 1 | Geopolymers, Inorganic Polymers, Hybrid Organic-Inorganic Polymer Materials |
| Focused Session 2 | Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites |
| Focused Session 3 | Next Generation Technologies for Innovative Surface Coatings |
| Focused Session 4 | Advanced (Ceramic) Materials and Processing for Photonics and Energy |
| Special Session | European Union – USA Engineering Ceramics Summit |
| Special Session | Global Young Investigators Forum |

The proceedings papers from this conference will appear in nine issues of the 2012 Ceramic Engineering & Science Proceedings (CESP); Volume 33, Issues 2-10, 2012 as listed below.

- Mechanical Properties and Performance of Engineering Ceramics and Composites VII, CESP Volume 33, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Materials for Extreme Environments II, CESP Volume 33, Issue 3 (includes papers from Symposia 2 and 12 and Focused Session 3)
- Advances in Solid Oxide Fuel Cells VIII, CESP Volume 33, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VIII, CESP Volume 33, Issue 5 (includes papers from Symposium 4)

- Advances in Bioceramics and Porous Ceramics V, CESP Volume 33, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology VI, CESP Volume 33, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials VI, CESP Volume 33, Issue 8 (includes papers from Symposium 8)
- Ceramic Materials for Energy Applications II, CESP Volume 33, Issue 9 (includes papers from Symposia 6, 13, and 14)
- Developments in Strategic Materials and Computational Design III, CESP Volume 33, Issue 10 (includes papers from Symposium 10 and from Focused Sessions 1, 2, and 4)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.

ACerS and the ECD invite you to attend the 37th International Conference on Advanced Ceramics and Composites (<http://www.ceramics.org/daytona2013>) January 27 to February 1, 2013 in Daytona Beach, Florida.

MICHAEL HALBIG AND SANJAY MATHUR
Volume Editors
July 2012

Contents

| | |
|--|-----|
| Preface | vii |
| Introduction | ix |
| Nanostructured Coatings by Cluster Beam Deposition: Method and Applications | 1 |
| Emanuele Barborini, Simone Vinati, and Roberta Carbone | |
| In-Situ Growth of Carbon Nanotubes in Three Dimensional Needle-Punched Carbon Fabrics and Hybrid Enhancement to C/SiC Composites | 15 |
| Jianbao Hu, Shaoming Dong, Xiangyu Zhang, Bo Lu, Zhihui Hu, Jinshan Yang, Qinggang Li, and Bin Wu | |
| Boron Nitride Nanotubes Grown on Commercial Silicon Carbide Fiber Tow and Fabric | 21 |
| Janet Hurst | |
| A New Greener Synthetic Route to Cadmium/Lead Selenide and Telluride Nanoparticles | 31 |
| Neerish Revaprasadu | |
| Nanowire Based Solar Cell on Multilayer Transparent Conducting Films | 45 |
| D. R. Sahu, Jow-Lay Huang, and S. Mathur | |
| Antimicrobial Properties of Copper and Silver Loaded Silica Nanomaterials | 55 |
| Pavithra Mani prasad, Roseline Menezes, Jenelle Suarez, and Swadeshmukul Santra | |

| | |
|--|-----|
| Hot Wire and Spark Pyrolysis as Simple New Routes to Silicon Nanoparticle Synthesis M. R. Scriba, D. T. Britton, and M. Härting | 69 |
| Plasma-Assisted Chemical Vapor Deposition of Fe:TiO ₂ Films for Photoelectrochemical Hydrogen Production Andreas Mettenbörger, Vanessa Merod, Aadesh P. Singh, Helge Lemmetyinen, and Sanjay Mathur | 81 |
| CNT Based Nanocomposite Strain Sensor for Structural Health Monitoring A. K. Singh | 89 |
| Photocatalytic Degradation of Waste Liquid from Biomass Gasification in Supercritical Water with Simultaneous Hydrogen Production over CdS Sensitized Na ₂ Ti ₂ O ₄ (OH) ₂ Wendong Tang, Dengwei Jing, Simao Guo, Jiarong Yin, and Liejin Guo | 105 |
| Recent Advances in Membrane Development for CO ₂ Free Fossil Power Plants Tim Van Gestel, Stefan Baumann, Mariya Ivanova, Wilhelm Meulenberg, and Hans Peter Buchkremer | 115 |
| Electrospinning of Nanocomposite Scaffolds for Bone Tissue Engineering: Emitting Electrode Polarity and Charge Retention Ho-Wang Tong and Min Wang | 127 |
| Graphitic Carbon Nitride Modified by Silicon for Improved Visible-Light-Driven Photocatalytic Hydrogen Production Po Wu, Jinwen Shi, Jie Chen, Bin Wang, and Liejin Guo | 137 |
| Fabrication of CdS/ZnO Core-Shell Nanofibers By Electrospinning and Their Photocatalytic Activity Yan Wei and Yang Guorui | 149 |
| Author Index | 161 |

NANOSTRUCTURED COATINGS BY CLUSTER BEAM DEPOSITION: METHOD AND APPLICATIONS

Emanuele Barborini, Simone Vinati, and Roberta Carbone

Tethis SpA

Milan, Italy

ABSTRACT

One of the key issues to be addressed in order to exploit nanomaterial peculiar properties is the way devices, and surfaces in general, can be functionalized by nanomaterials. To allow the jump beyond lab-scale, deposition techniques are asked to fulfill requirements such as reliability and repeatability, batch deposition, scalability, compatibility with micromachining techniques.

Here we show how supersonic cluster beam deposition, based on pulsed microplasma cluster source, may answer these requests, while offering at the same time a wide library of available nanomaterials, including carbon, oxides, and noble metals. The growth of nanostructured functional coating takes place directly onto whatever surface exposed in front of the cluster beam. Cluster soft-assembling generates nanoporosity and, as a consequence, coatings with large specific surface, which are particularly suited for applications where interaction with liquid solutions or gas-phase atmospheres has to be favored.

Results on the integration of nanostructured coatings into devices with applicative purposes in sensing field and in biotech field, will be reported. They include gas sensing, stretch sensing, protein adsorption, cell adhesion, and selective capture of peptides, as examples of functions that may be added to devices by cluster beam deposition of nanomaterials.

INTRODUCTION

One of the most important ways to exploit the peculiar properties of nanomaterials is their integration into devices or generally onto surfaces, in form of functional coatings. For example, devices with applications in the field of energy storage/production, such as supercapacitors, fuel cells, or electrochemical photovoltaic cells, may enhance their performances by using high specific surface nanostructured coatings deposited onto their electrodes, in order to favor the interaction with the liquid or gas phases.¹⁻⁴ Usually, the synthesis of the precursors of the nanostructured coatings and the integration in devices are two well-separated production steps, whose characteristics may frequently limit the range of the applications of the nanomaterials from a given synthesis route. For example, the use of nanomaterials from wet-chemistry synthesis routes as active sensing layer into micromachined gas sensing platforms, is hampered on one side by the mechanical delicacy of micromachined parts, and on the other side by the presence of solvents in precursor material.⁵⁻⁶ Moreover, nanomaterials from synthesis routes that require high temperature calcination step are incompatible with thermolabile substrates, such as polymers. Finally, the functionalization of devices in batch requires patterned deposition with suitable lateral resolution, in order to deposit nanomaterials onto the proper functional area, within each single device. Although photolithography is the common approach to fulfill this task, it raises non-trivial issues in the case of micromachined devices.⁶ Hence, a demand does exist of alternative methods for the production of nano-enhanced systems, where nanoparticle synthesis, manipulation, and integration steps are synergic parts of a unique process, overcoming most of the limitations of current approaches.

Here we describe a gas-phase method, based on supersonic cluster beams, for the functionalization of surfaces and devices with nanomaterials that may offer interesting opportunities with respect to nanomaterial integration issue. The first part of the paper will report on the deposition technique, with particular emphasis on cluster source. Results of morphological and structural characterization of cluster-assembled materials by means of electron microscopy and scanning probe

techniques will be also reported. The second part of the paper will show some relevant examples of applications of nanostructured materials by supersonic cluster beam deposition within various applicative fields in sensing and biotech, such as chemical and mechanical sensing, protein adsorption, cell adhesion, and peptide selective capture.

EXPERIMENTAL

Supersonic Cluster Beam Deposition (SCBD)

As shown in figure 1, SCBD apparatus basically consists of two vacuum chambers, each having its own pumping system. The cluster source is connected to the first chamber, which is named expansion chamber. Driven by pressure difference between source inner and expansion chamber, a supersonic expansion of an inert gas (typically Argon), takes place through the source nozzle, carrying clusters out from production region (source inner), towards deposition region. At odd with respect to effusive sources, supersonic expansion causes the cluster beam to concentrate within a divergence of few degrees, ensuring that a large fraction of the material produced into the source is directed towards deposition region.

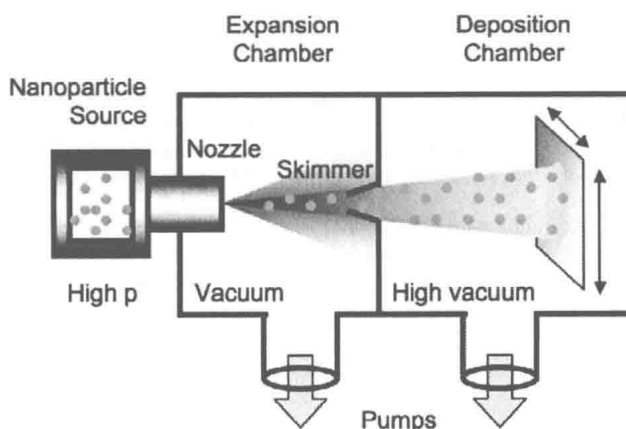


Figure 1. Scheme of the apparatus for supersonic cluster beam deposition. Arrows in deposition chamber indicate substrate rastering for large area depositions.

The second chamber is separated from the expansion chamber by means of a collimator with aerodynamic shape (skimmer), which removes most of the gas load due to cluster carrier, allowing only the central portion of the cluster beam to reach deposition region. In the case that the growth of cluster-assembled material should be performed in ultra-high-vacuum (UHV) conditions, as in Surface Science experiments, the number of vacuum chambers may be increased (according to the so-called differential vacuum approach) since beam collimation anyway provides for an adequate material collection.

If the coverage of areas exceeding the size of the cluster beam spot, which is typically few cm^2 , is needed, substrate rastering may be adopted: exploiting motorized sample holder, substrate scanning in front of the cluster beam is operated, so that areas extending up to few hundreds of cm^2 can be processed.

Pulsed Microplasma Cluster Source (PMCS)

Although various cluster sources adopt supersonic expansion for the production of their cluster beam, such as Laser Vaporization Sources or Pulsed Arc Sources⁷, we will focus here on Pulsed Microplasma Cluster Source (PMCS). PMCS is a rather recent system that we engineered and scaled-up in the last decade, and used to explore various applications of nanostructured coatings, as described in Sensing and Biotech Results section.

As first described in⁸ and successively in⁷⁻⁹, PMCS consists of a cylindrical ceramic element, hosting a suitable reaction cavity. A solenoid pulsed valve for the injection of the inert carrier gas closes the back side of the cavity, while a nozzle closes the front side. The solenoid valve is typically backed with a 50 bar gas line, and operates at an opening time of about two hundreds of microseconds. A channel perpendicular to cavity axis holds the metal rod-shaped target, which is used for clusters production. In presence of the inert gas pulse from solenoid valve, the metal target is negatively pulsed by means of a high-voltage, high-current dedicated power supply. An electric discharge from grounded nozzle to negatively-pulsed target takes place, generating a plasma of the inert gas. Plasma jet impinges on target surface and vaporizes part of it. Then, ablated atoms thermalize and condense to form clusters.

The pressure difference between the source cavity and the vacuum chamber where the source is faced (expansion chamber) causes the expansion across the source nozzle of the clusters-inert gas mixture, generating the supersonic clusters beam. The supersonic expansion accelerates clusters at a kinetic energy of few tenths of eV per atom, thus promoting an adequate adhesion of the resulting cluster-assembled coating while preserving the cluster original structure and avoiding any significant damage or heating of the substrate.

If supersonic expansion is forced through aerodynamic lenses¹⁰, it is possible to obtain a highly collimated (divergence <1 deg) and intense cluster beam (aerodynamic focusing). By exploiting this property, patterned deposition of nanostructured coatings with sub-micrometric lateral resolution can be produced by non-contact stencil mask.¹¹ This feature marks a fundamental difference with respect to other gas-phase deposition techniques, since it allows for the easy integration of nanomaterials in functional areas of micro electro mechanical systems (MEMS) and micromachined platforms in general, avoiding photolithographic approach (see Gas sensing section below).

COATING CHARACTERIZATION

Atomic Force Microscopy

Surface morphology of cluster-assembled coatings has been studied by atomic force microscopy (AFM). Four examples are reported in figure 2, where the surface morphology of Ti, Hf, Zr, Fe nanostructured oxides is shown. Similar morphological features are observed in almost every nanostructured coating obtained by SCBD-PMCS. Therefore, we suppose that they can be ascribed to the deposition process in itself, and in particular to the low kinetic energy and limited diffusion of nanoparticles at the impact with the substrate, determining ballistic regime growth^{7,12}, which is characterized by nanoscale porosity, poorly-connected and non-compact structures with lower density respect to bulk and a surface roughness increasing with thickness.

AFM has been also adopted to evaluate the size distribution of coating precursors. To this purpose, very low coverage samples, with isolated nanoparticles, were deposited. Careful substrate preparation before deposition, as well as reference samples not exposed to the cluster beam, were adopted to favor artifacts identification/elimination in AFM images. Statistic of in-plane diameters was compared with statistic of heights, in order to identify the nanoparticle subset characterized by the height-diameter relation of spheroidal objects, and rule out non-spheroidal ones. In addition, size over-estimation due to AFM tip radius was avoided by limiting the counts of final size distribution to the heights of spheroidal objects subset. Size distributions were found to be lognormal, as expected for

nanoparticles growth by gas-phase monomer aggregation into PMCS, as reported in¹³ in the case of gold nanoparticles.

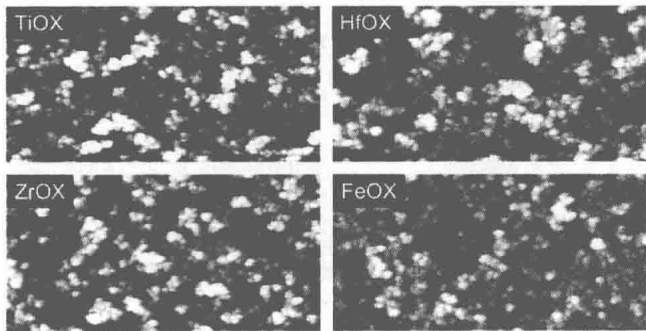


Figure 2. AFM images showing the surface morphology of four nanostructured oxides, with thicknesses around 200 nm. Each image has a size of $1 \times 2 \mu\text{m}^2$. It clearly appears that surface morphologies are very similar among the different oxides, a feature that is ascribable to growth dynamics of deposition process in itself.

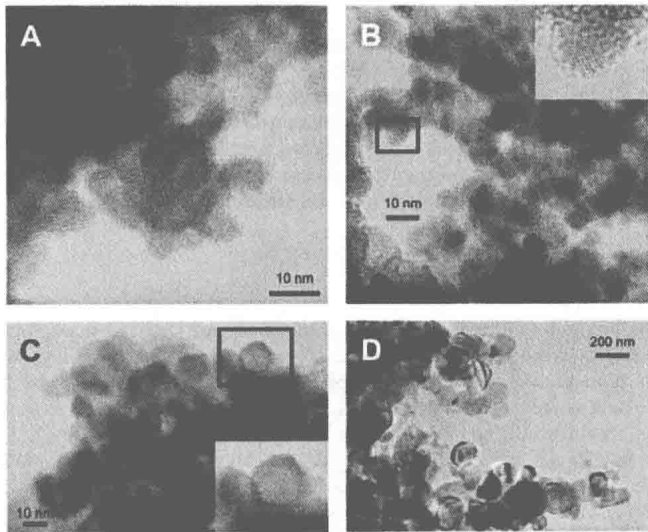


Figure 3. TEM images showing the nanostructure of as-deposited WO_3 film (A) and its evolution after thermal treatments at 200, 400, and 800 °C (B, C, D, respectively). Absence of lattice fringes inside nanoparticles of as-deposited film (A) indicates an amorphous structure. Annealing causes the evolution of nanoparticle structure toward crystalline order, which is almost completely reached after 400 °C. A progressive increase of crystal size is also observed, however nanoporous structure is preserved up to 800 °C. Reprinted with permission from¹⁴.