

Innovative Processing and Synthesis of Ceramics, Glasses, and Composites V

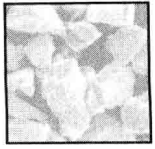
Edited by

J.P. Singh

Narottam P. Bansal

Amit Bandyopadhyay

Ceramic
Transactions
Volume 129



**Ceramic
Transactions**
Volume 129

Innovative Processing and Synthesis of Ceramics, Glasses, and Composites V

江苏工业学院图书馆
藏书章

*Proceedings of the Innovative Processing and Synthesis of
Ceramics, Glasses, and Composites symposium held at the
103rd Annual Meeting of The American Ceramic Society, April
22-25, 2001, in Indianapolis, Indiana, USA*

Edited by

J.P. Singh

Argonne National Laboratory

Narottam P. Bansal

National Aeronautics and Space
Administration Glenn Research Center

Amit Bandyopadhyay

Washington State University

Published by

The American Ceramic Society
735 Ceramic Place
Westerville, Ohio 43081
www.ceramics.org

Proceedings of the Innovative Processing and Synthesis of Ceramics, Glasses, and Composites symposium held at the 103rd Annual Meeting of The American Ceramic Society, April 22–25, 2001, in Indianapolis, Indiana, USA.

Copyright 2002, The American Ceramic Society. All rights reserved.

Statements of fact and opinion are the responsibility of the authors alone and do not imply an opinion on the part of the officers, staff, or members of The American Ceramic Society. The American Ceramic Society assumes no responsibility for the statements and opinions advanced by the contributors to its publications or by the speakers at its programs. Registered names and trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by the law.

No part of this book may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, microfilming, recording, or otherwise, without written permission from the publisher.

Authorization to photocopy for internal or personal use beyond the limits of Sections 107 and 108 of the U.S. Copyright Law is granted by the American Ceramic Society, provided that the appropriate fee is paid directly to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923 USA, www.copyright.com. Prior to photocopying items for educational classroom use, please contact Copyright Clearance Center, Inc.

This consent does not extend to copying items for general distribution or for advertising or promotional purposes or to republishing items in whole or in part in any work in any format.

Please direct republication or special copying permission requests to Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923 USA 978-750-8400; www.copyright.com.

Cover photo: “The SEM images show typical morphology of the spray particles used in this work,” is courtesy of R. Gadow, A. Killinger, and C. Li, and appears as figure 4a in the paper “Plasma Sprayed Ceramic Coatings on Glass and Glass Ceramic Substrates,” which begins on page 15.

Library of Congress Cataloging-in-Publication Data

A CIP record for this book is available from the Library of Congress.

For information on ordering titles published by The American Ceramic Society, or to request a publications catalog, please call 614-794-5890.

Printed in the United States of America.

4 3 2 1–05 04 03 02

ISSN 1042-1122

ISBN 1-57498-137-4

Innovative Processing and Synthesis of Ceramics, Glasses, and Composites V

Related titles published by The American Ceramic Society:

Boing-Boing the Bionic Cat and the Jewel Thief

By Larry L. Hench

©2001, ISBN 1-57498-129-3

*Innovative Processing and Synthesis of Ceramics, Glasses, and Composites IV
(Ceramic Transactions, Volume 115)*

Edited by Narottam P. Bansal and J.P. Singh

©2000, ISBN 1-57498-111-0

*Innovative Processing and Synthesis of Ceramics, Glasses, and Composites III
(Ceramic Transactions Volume 108)*

Edited by J.P. Singh, Narottam P. Bansal, and Koichi Niihara

©2000, ISBN 1-57498-095-5

Advances in Ceramic Matrix Composites V (Ceramic Transactions, Volume 103)

Edited by Narottam P. Bansal, J.P. Singh, and Ersan Ustundag

©2000, ISBN 1-57498-089-0

The Magic of Ceramics

By David W. Richerson

©2000, ISBN 1-57498-050-5

Boing-Boing the Bionic Cat

By Larry L. Hench

©2000, ISBN 1-57498-109-9

Ceramic Innovations in the 20th Century

Edited by John B. Wachtman Jr.

©1999, ISBN 1-57498-093-9

Advances in Ceramic Matrix Composites IV (Ceramic Transactions, Volume 96)

Edited by J.P. Singh and Narottam P. Bansal

©1999, ISBN 1-57498-059-9

*Innovative Processing and Synthesis of Ceramics, Glasses, and Composites II
(Ceramic Transactions, Volume 94)*

Edited by Narottam P. Bansal and J.P. Singh

©1999, ISBN 1-57498-060-2

*Innovative Processing and Synthesis of Ceramics, Glasses, and Composites
(Ceramic Transactions, Volume 85)*

Edited by Narottam P. Bansal, Kathryn V. Logan, and J.P. Singh

©1998, ISBN 1-57498-030-0

Advances in Ceramic Matrix Composites III (Ceramic Transactions, Volume 74)

Edited by Narottam P. Bansal and J.P. Singh

©1996, ISBN 1-57498-020-3

For information on ordering titles published by The American Ceramic Society, or to request a publications catalog, please contact our Customer Service Department at 614-794-5890 (phone), 614-794-5892 (fax), <customersvc@acers.org> (e-mail), or write to Customer Service Department, 735 Ceramic Place, Westerville, OH 43081, USA.

Visit our on-line book catalog at <www.ceramics.org>.



Preface

This volume contains papers presented at a symposium on Innovative Processing and Synthesis of Ceramics, Glasses and Composites held during the 103rd Annual Meeting and Exposition of the American Ceramic Society in Indianapolis, April 22-25, 2001. This symposium provided an international forum for scientists and engineers to discuss all aspects of processing and synthesis of ceramics, glasses and composites. A total of 114 papers, including invited talks, oral presentations, and posters, were presented from 17 countries (the United States, Belgium, Brazil, Canada, Germany, Iran, Israel, Italy, Japan, Mexico, the People's Republic of China, Republic of Korea, Spain, Switzerland, Taiwan, United Kingdom, and Venezuela). The speakers represented universities, industry, and research laboratories.

This volume contains 18 invited and contributed papers, all peer-reviewed according to American Ceramic Society procedures. The latest developments in processing and characterization are covered: CVD/CVI and plasma technology, gas infiltration and polymer processing, rheological behavior, mechanical alloying, reaction forming, functionally graded materials and coatings, laminated object manufacturing, and electronic and magnetic materials. All of the most important aspects necessary for understanding and further development of ceramic processing and characterization are discussed.

The organizers are grateful to all participants and session chairs for their time and effort, to authors for their timely submissions and revisions of the manuscripts, and to reviewers for their valuable comments and suggestions; without the contributions of all involved, this volume would not have been possible. Financial support from the American Ceramic Society is gratefully acknowledged. Thanks are due to the staff of the Meetings and Publications Department of the American Ceramic Society for their tireless efforts. Especially, we greatly appreciate the helpful assistance and cooperation of Sarah Godby throughout the production process of this volume.

We hope that this volume will serve as a useful reference for professionals working in the field of synthesis and processing of ceramics, glasses, and composites.

J. P. Singh

Narottam P. Bansal

Amit Bandyopadhyay

Contents

Preface	ix
---------------	----

CVD/CVI and Plasma Technology

Cubic and Tetragonal Hafnium Oxide Films Prepared by Ion-Beam-Assisted Deposition	3
R. R. Manory, I. Shimizu, T. Mori, S. Miyake, H. Saito, G. Kimmel, and T. Tanaka	

Plasma-Sprayed Ceramic Coatings on Glass and Glass Ceramic Substrates.	15
R. Gadow, A. Killinger, and C. Li	

Gas Infiltration and Preceramic Polymer Processing

Manufacturing of Biomorphic SiC Ceramics by Gas Phase Infiltration of Wood.	33
E. Vogli, C. Zollfrank, H. Sieber, P. Greil, and J. Mukerji	

Manufacturing of Anisotropic Ceramics from Preceramic Polymer Infiltrated Wood.	43
C. Zollfrank, R. Kladny, H. Sieber, P. Greil, and G. Motz	

Rheological Behavior

Modeling the Dynamic Rheological Behavior of AGAR-Based Aqueous Binders.	53
K. C. Labropoulos, D. E. Niesz, and S. C. Danforth	

Mechanical Alloying

Effects of Alloying with Nb, Re, and Al on Yield Strength of MoSi ₂	69
A. A. Sharif, A. Misra, J. J. Petrovic, and T. E. Mitchell	

Reaction Forming

<i>In situ</i> Synthesis of Nonoxide-Boron Nitride (NOBN) Composites	83
--	----

G. J. Zhang, J. F. Yang, T. Ohji, and S. Kanzaki

Fabrication of Lightweight Oxide/Intermetallic Composites at 1000°C by the Displacive Compensation of Porosity (DCP) Method	93
---	----

P. J. Wurm, P. Kumar, K. D. Ralston, M. J. Mills, and K. H. Sandhage

Microstructure and Mechanical Properties of SiAlON Ceramics with Porous Structure	103
---	-----

J. Yang, Y. Beppu, G. J. Zhang, and T. Ohji

Functionally Graded Materials & Coatings

Functionally Graded Porosity in Ceramics—Analysis with High Resolution Computed Tomography	113
--	-----

J. Goebbels, G. Weidemann, R. Ditttrich, M. Mangler, and G. Tomandl

Novel Processing for Combined Coatings with Dry Lubrication Ability	125
---	-----

R. Gadow and D. Scherer

Ceramic Coatings on Fiber Woven Fabrics for Lightweight Ballistic Protection	137
--	-----

K. V. Niessen and R. Gadow

Laminated Object Manufacturing

The Effect of Sheetstock on the Layered Manufacturing of a Telescoping Ceramic Actuator	153
---	-----

A. A. Bender and R. J. Rayne

Electronic and Magnetic Materials

Binder Removal by Supercritical Extraction from BaTiO ₃ -Pt Multilayer Ceramic Capacitors	165
--	-----

S. J. Lombardo, R. V. Shende, and D. S. Krueger

Processing and Characterization of PZT and PLZT Thick Films. 175
O. Huang, A. Bandyopadhyay, and S. Bose

Micromachining of PZT-Based MEMS 187
T. B. Myers, S. Bose, A. Bandyopadhyay, and J. D. Fraser

Templated Grain Growth of Lead Metaniobate Ceramics by Solid Freeform Fabrication. 199
K. Nonaka, M. Allahverdi, and A. Safari

Investigation of Ni-Cu-Zn Ferrite with High Performance Derived from Nanoferrite Powders 211
X. Wang, W. Qu, L. Li, Z. Gui, and J. Zhou

Index 219

CVD/CVI and Plasma Technology

CUBIC AND TETRAGONAL HAFNIUM OXIDE FILMS PREPARED BY ION BEAM ASSISTED DEPOSITION

Rafael R. Manory, Ipppei Shimizu,
Takanori Mori and Shoji Miyake
Joining and Welding Research Institute
Osaka University, 11-1 Mihagaoka,
Ibaraki, Osaka 547-0067 Japan

Hidenori Saito
Kanagawa High-Technology
Foundation (KTF), 3-2-1 Sakado
Takatsu-ku, Kawasaki-shi
Kanagawa 213-0012 Japan

Giora Kimmel
Dept. of Materials Engineering,
Ben Gurion University of the Negev
Beer-Sheva, 84307 Israel

Takeo Tanaka
Dept. of Mechanical Engineering
Osaka Sangyo University
3-1-1 Nakagaito, Daito, Osaka,
574, Japan

ABSTRACT

HfO₂ films were prepared by ion beam assisted deposition (IBAD) of hafnium with simultaneous bombardment with oxygen ions, accelerated between 1-20keV. The ratio between the hafnium arrival rate and the oxygen ion dose, (transport ratio, TR) was varied between 0.5 and 10. Structure and composition were characterized using XRD, XPS, RBS, EPMA.

Two unexpected structures were observed with variation in parameters, a cubic CaF₂-type structure with a parameter of about 0.412nm and a new tetragonal structure, believed to be different from the high temperature HfO₂ structure. The composition of the films was found to be under-stoichiometric, with Hf/O ratio around 1.5. The new tetragonal structure appears to be correlated to low oxygen content, below 1.5. Film orientation could be controlled by varying the substrate rotation during deposition.

INTRODUCTION

Hafnium dioxide has a number of isomorphs and has been the topic of numerous studies. At room temperature the equilibrium phase of hafnia is monoclinic baddeleyite,¹⁻³ which has the lowest free energy of formation and the largest volume. The effects of stoichiometry and temperature variations under atmospheric and higher pressures have been studied by various authors, and the phase diagram of Hf-O has been determined.¹⁻³ There is some solubility of O in Hf, but the only oxide phase identified in the phase diagram at room temperature

To the extent authorized under the laws of the United States of America, all copyright interests in this publication are the property of The American Ceramic Society. Any duplication, reproduction, or republication of this publication or any part thereof, without the express written consent of The American Ceramic Society or fee paid to the Copyright Clearance Center, is prohibited.

was HfO_2 , with a phase boundary at about 63.5 at% oxygen.³ At about 1300K, monoclinic HfO_2 transforms into a tetragonal structure and at about 2700K into a cubic structure,^{3,4} of the CaF_2 -type⁴. It is interesting to note that Passerini⁵ identified the CaF_2 structure in the HfO_2 - CeO_2 system as early as 1930. With increasing pressure, densification of monoclinic HfO_2 occurs by transformation into a number of orthorhombic phases, which have been closely studied and mapped.^{1,2,6,7}

With the exception of the main phases obtained at atmospheric pressure, other phases were observed in bulk material only under high-pressure conditions. The high-density phases obtained under high-pressure conditions appear to have elastic moduli of the order of 145GPa and are therefore considered among the super-hard materials⁸.

The main interest however in this material is for optical coatings. It presents a relatively high laser damage threshold due to its high melting point, thermal and chemical stability^{9,10} and a large transparent range from the IR to the UV (0.22-12 μm), with a relatively high refractive index,¹⁰ and is also relatively easy to obtain by evaporation. In view of these properties, a number of techniques were used to produce such films, including sol-gel¹¹, atomic layer deposition (ALD)¹², in addition to vacuum deposition methods.

Among the various attempts to obtain high quality optical films, ion beam assisted deposition (IBAD) has also been used in a number of studies,⁹⁻¹³ with various ion sources, sometimes using ionic species other than oxygen. In connection to the present work, is worth noting that non-stoichiometry of the HfO_x films has been reported¹⁴, but without effects on the structure.

The cubic and tetragonal high temperature structures have been sometimes observed in thin films in small amounts alongside the monoclinic structure. Aarik et al.¹² have reported the presence of the orthorhombic phase in films obtained by the ALD method at 500°C, whereas Ritala et al.^{15,16} have observed weak peaks of a tetragonal structure. Recently, Aarik et al.¹⁷ have reported the presence of cubic nano-crystallites on the surface layers of monoclinic HfO_2 films grown by the ALD method at temperatures in the vicinity of 900°C.

The work presented here was undertaken in an attempt to explore the effects of ion bombardment on phase transitions and properties of thin HfO_2 films deposited by IBAD at ion energies of 1-20 keV, significantly higher than ion acceleration energies used in other^{9,13,14} IBAD works. The bombarding ion was oxygen, but we varied the transport ratio (TR), defined as the ratio between the oxygen flow-rate, and the hafnium evaporation rate. The parameters varied included transport ratio, ion energy, alloying with Ce, substrate cooling and substrate rotation speed. In contradiction with other reports, we obtained films consisting not of a monoclinic

phase with some other high temperature phase, but entirely, or almost entirely of either cubic or tetragonal phase, (which appears to belong to a different space group than the high temperature tetragonal structure of hafnia).

TABLE I – List of samples and experimental conditions

Sample	Ion Energy	T.R.	Deposition rate	Rotation rate	Composition (O/Hf ratio)	
	keV	---	---	sec/pass	XPS	EPMA
1	20	5	3.5	low	1.30	1.44
2	20	1	0.7	low	1.55	1.54
3	20	10	5.3	low	1.47	1.44
4	20	0.5	0.3	low	1.71	---
6	20	4	2.8	low	---	---
7	20	2	1.3	low	---	---
8	1.0	5	1.8	low	1.74	---
9	10	5	2.9	low	1.52	---
11	5	5	2.7	low	1.72	---
20*	20	5	3.5	low	---	1.56
14	20	5	Hf = 3.8, Ce = 0.3	low	---	Ce/(Hf+Ce)=0.025
15	1	5	Hf = 1.7, Ce = 0.2	low	---	Ce/(Hf+Ce)=0.021
16	10	5	Hf = 3.9, Ce = 0.5	low	---	---
37	20	5	3.4	87	---	---
36	20	5	3.4	50	---	---
28	20	5	3.3	20	---	1.27
35	20	5	3.3	0	---	1.16

*This sample was deposited without water-cooling the substrate.

EXPERIMENTAL

A compact IBAD system with a bucket-type 2.45-GHz electron-cyclotron-resonance ion source and an electron beam evaporation source was used for the preparation of the HfO_2 films. The basic details of the ion source have been described elsewhere.^{18,19} The acceleration voltage of the extracted oxygen ions was varied in the range of 1-20 kV. The ion current density measured with a Faraday cup was typically $26\text{--}51 \mu\text{A}/\text{cm}^2$. The base pressure, evacuated with a 1500-l/s cryo-pump was $1\text{--}2 \times 10^{-6}$ torr. The working pressure of oxygen during the ion source operation was $1\text{--}3 \times 10^{-4}$ torr due to gas flow from the ion source. The substrate was maintained at a low temperature by water-cooling the plate under

the substrate holder. The films were obtained on Si (100) wafers by depositing Hf vapor (from a target with purity 98 at%, with the major impurity being Zr) under simultaneous bombardment with oxygen ions. The incidence angle of the oxygen ion beam was normal to the substrate and the hafnium vapor reached the substrate at an angle of approximately 45° from normal. The transport-rate ratio of was varied in the range of 0.5-10. Typical film thickness was in the range of 400-600nm, as measured by surface profilometry. The substrate was rotated during deposition at various speeds varying between 0-3 rpm. (One rotation in 20 sec. is 'high rate' and in 90 sec is considered 'slow').

X-ray diffraction (XRD) data was collected using Cu radiation in a Rigaku Miniflex apparatus at 30 kV-15 mA, with a Ni filter, in the $\theta/2\theta$ mode. The chemical composition was measured using electron probe microanalysis (EPMA). Selected samples were analyzed by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering (RBS). For standard HfO₂, a powder made by Alfa-Johnson Matthey GmbH. (Puratronic - 99.988% purity), was used.

Microstructures were obtained (courtesy of Kanagawa High-Technology Foundation (KTF)) using a field emission scanning electron microscope (FE-SEM) capable of ultra high magnification (up to $\times 10^5$).

RESULTS AND DISCUSSION

The experimental conditions for the films discussed here are given in Table I (organized in order of parameter variation). Figure 1a presents the XRD spectrum of sample #1 (20 keV, TR=5). Three strong peaks at about 30, 35 and 50° are observed, with additional small peaks at about 40 and 60°. The three strong peaks together do not belong to any of the ICDD cards for HfO₂ structures. This spectrum, with the exception of the peak at 40° appeared to be typical of a cubic structure, fitting the CaF₂ structure reported by Passerini⁵, and also mentioned in the Pearson handbook.²⁰ A calculated spectrum for such a structure with $a_0=0.506\text{nm}$ is shown in Fig. 1b.

The peaks at 40° and 55° in Fig. 1a are broader than those at 30° and 35° (full width at half maximum -FWHM- is 0.52, compared to 0.32 for the latter two). The broad peaks were de-convoluted using the Gaussian formula and it was determined that this film has a tetragonal rather than cubic structure, with the parameters $a=0.5055$ and $c=0.5111\text{ nm}$ (c/a ratio 1.011). The calculated spectrum of this structure is presented in Fig.1c. As can be observed, this spectrum fits well the spectrum shown in Fig. 1a. The c/a ratio in this structure differs from the value of 1.021 of the normal tetragonal hafnia structure of high-temperature (ICDD card 08-0342). The Miller indices listed in the ICDD card do not correspond to those observed in our film, and this fact, together with the change in the c/a ratio

this leads us to believe that the structure presented here is different from the tetragonal high temperature HfO_2 phase.

On the other hand, by varying ion energy we could obtain films exhibiting the cubic structure. The XRD spectrum of sample no. 8 (1keV, TR5) is shown in Fig. 1d. The additional peak at 40° does not appear here and this spectrum is similar to the cubic XRD profile of Fig. 1b.

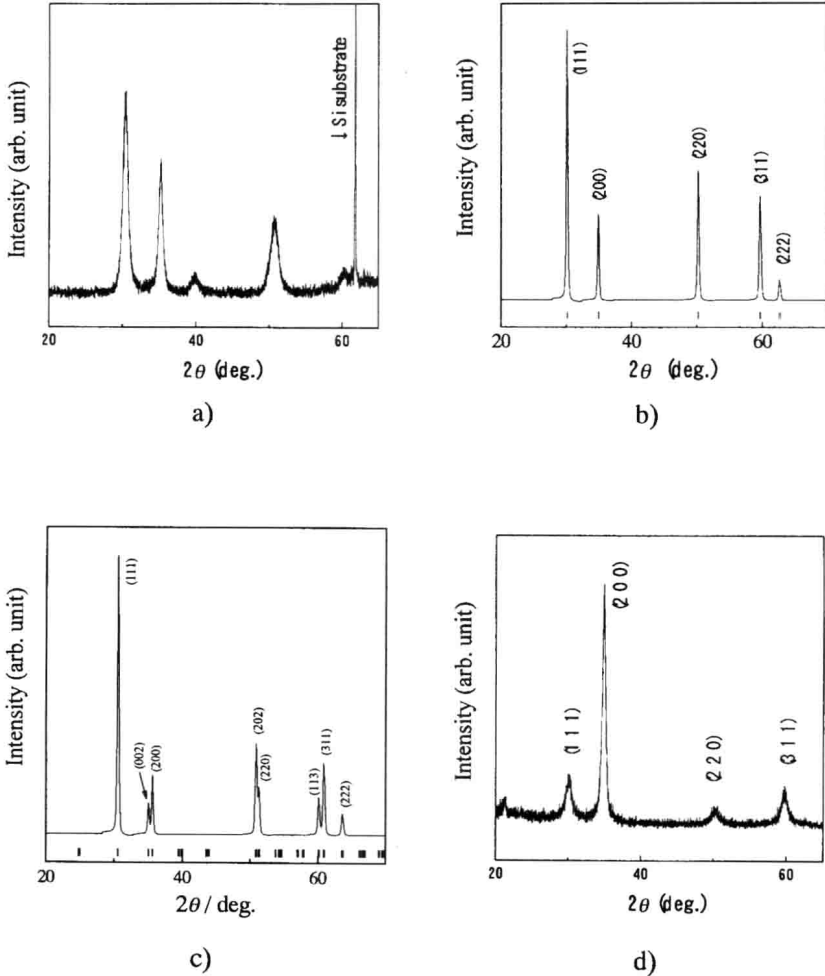


Figure 1. XRD spectra. a) Sample #1; b) Calculated spectrum of the CaF_2 structure with $a_0=0.506\text{nm}$; c) calculated spectrum of a tetragonal structure fitting Fig. 1a; d) Spectrum of sample #8, fitting the calculated cubic model of Fig. 1b.

A film with a monoclinic structure is shown in Fig. 2, where the XRD spectrum of sample no. 7 is compared to a standard sample for monoclinic HfO_2 . The film also presents a certain degree of preferred orientation.

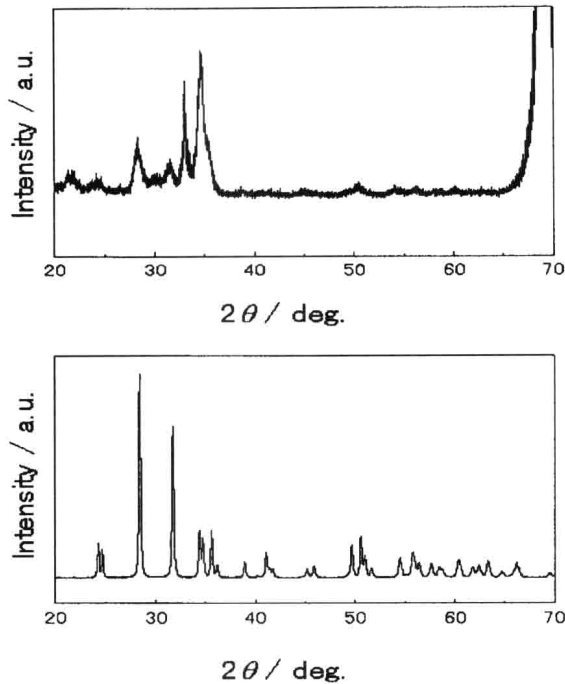


Fig. 2. XRD spectrum of sample #7 (20keV, T.R.2) (top), and comparison with the spectrum of standard monoclinic HfO_2 powder (bottom). The deposited film also contains a second phase –(either cubic or tetragonal, oriented (200)).

Figure 3 presents high-resolution FE-SEM micrographs of three types of films obtained with variation of parameters- samples nos.1, 7 and 14, which are almost entirely tetragonal monoclinic and cubic (oriented), respectively. It should be noted that a small component of a second phase is always present in these samples. All three samples present a columnar structure, but the grains and their spacing are very different. The mechanical properties of these samples are discussed elsewhere²¹. Sample no. 1 (Fig 3 -top) presents a very dense columnar structure and a smooth surface, whereas the monoclinic sample no. 7 (Fig.3-middle) shows