

Science and Technology of Electroceramic Thin Films

Edited by

Orlando Auciello and Rainer Waser

NATO ASI Series

Science and Technology of Electroceramic Thin Films

edited by

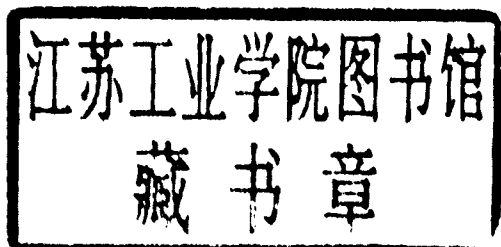
Orlando Auciello

MCNC,
Electronics Technology Division,
Research Triangle Park, North Carolina, U.S.A.

and

Rainer Waser

Institut für Werkstoffe der Elektrotechnik,
RWTH Aachen University of Technology,
Aachen, Germany



Kluwer Academic Publishers

Dordrecht / Boston / London

Published in cooperation with NATO Scientific Affairs Division

Proceedings of the NATO Advanced Research Workshop on
Science and Technology of Electroceramic Thin Films
Villa del Mare, Italy
June 20–24, 1994

A C.I.P. Catalogue record for this book is available from the Library of Congress.

ISBN 0-7923-3332-2

Published by Kluwer Academic Publishers,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

Kluwer Academic Publishers incorporates the publishing programmes of
D. Reidel, Martinus Nijhoff, Dr W. Junk and MTP Press.

Sold and distributed in the U.S.A. and Canada
by Kluwer Academic Publishers,
101 Philip Drive, Norwell, MA 02061, U.S.A.

In all other countries, sold and distributed
by Kluwer Academic Publishers Group,
P.O. Box 322, 3300 AH Dordrecht, The Netherlands.

Printed on acid-free paper

All Rights Reserved

© 1995 Kluwer Academic Publishers and copyright holders as specified on appropriate pages within

No part of the material protected by this copyright notice may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying, recording or by any information storage and retrieval system, without written permission from the copyright owner.

Printed in the Netherlands

Science and Technology of Electroceramic Thin Films

NATO ASI Series

Advanced Science Institutes Series

A Series presenting the results of activities sponsored by the NATO Science Committee, which aims at the dissemination of advanced scientific and technological knowledge, with a view to strengthening links between scientific communities.

The Series is published by an international board of publishers in conjunction with the NATO Scientific Affairs Division

A Life Sciences	Plenum Publishing Corporation London and New York
B Physics	
C Mathematical and Physical Sciences	Kluwer Academic Publishers Dordrecht, Boston and London
D Behavioural and Social Sciences	
E Applied Sciences	
F Computer and Systems Sciences	Springer-Verlag Berlin, Heidelberg, New York, London, Paris and Tokyo
G Ecological Sciences	
H Cell Biology	
I Global Environmental Change	

PARTNERSHIP SUB-SERIES

1. Disarmament Technologies	Kluwer Academic Publishers
2. Environment	Springer-Verlag
3. High Technology	Kluwer Academic Publishers
4. Science and Technology Policy	Kluwer Academic Publishers
5. Computer Networking	Kluwer Academic Publishers

The Partnership Sub-Series incorporates activities undertaken in collaboration with NATO's Cooperation Partners, the countries of the CIS and Central and Eastern Europe, in Priority Areas of concern to those countries.

NATO-PCO-DATA BASE

The electronic index to the NATO ASI Series provides full bibliographical references (with keywords and/or abstracts) to more than 30000 contributions from international scientists published in all sections of the NATO ASI Series.

Access to the NATO-PCO-DATA BASE is possible in two ways:

- via online FILE 128 (NATO-PCO-DATA BASE) hosted by ESRIN, Via Galileo Galilei, I-00044 Frascati, Italy.
- via CD-ROM "NATO-PCO-DATA BASE" with user-friendly retrieval software in English, French and German (© WTV GmbH and DATAWARE Technologies Inc. 1989).

The CD-ROM can be ordered through any member of the Board of Publishers or through NATO-PCO, Overijse, Belgium.



Series E: Applied Sciences - Vol. 284

PREFACE

The basic and applied science of electroceramic thin films constitute one of the fast interdisciplinary evolving fields of research worldwide. A major driving force for the extensive research being performed in many Universities and Industrial and National Laboratories is the promise of applications of electroceramic thin films into a whole new generation of advanced microdevices that may revolutionize various technologies and create new multibillion dollar markets. Properties of electroceramic thin films that are being intensively investigated include electrical conductivity, ferroelectricity, piezoelectricity, pyroelectricity, electro-optic activity, and magnetism. Perhaps the most publicized application of electroceramics is that related to the new high temperature superconducting (HTSC) materials, which has been extensively discussed in numerous national and international conferences, including NATO/ASI's and ARW's. Less glamorously publicized applications, but as important as those of HTSC materials, are those involving the other properties mentioned above, which were the subject of this ARW. Investigation on ferroelectric thin films has experienced a tremendous development in recent years due to the advent of sophisticated film synthesis techniques and a substantial improvement in the understanding of the related materials science and implementation of films in various novel devices. A major driving force behind the progress in this interdisciplinary field of research is the promise of the development of a new generation of non-volatile memories with long endurance and fast access time that can overcome the problems encountered in the semiconductor non-volatile memory technology. Researchers have also rediscovered the utility of ferroelectric materials as high dielectric constant capacitors, which opens new possibilities for manufacturing planar, very high density DRAM memories. Ceramic conductors can be applied to ohmic, voltage-dependent, and thermally sensitive resistors; fast-ion conductors; and humidity and gas sensors. Piezoelectricity is being exploited in micromachines such as accelerometers, displacement transducers, and actuators such as those required for inkjet printers, for video-recording head positioning and for micromachining metals. Pyroelectricity can be utilized in the fabrication of high sensitivity infrared detectors, while electro-optic activity can be used in color filter devices, displays, image storage systems, and optical switches for integrated optical systems. The applications of electroceramic thin films mentioned above are only a part of a more extensive list, which indicates the relevance of these materials in the new technological era of a modern society. Most materials science and device issues related to electroceramic thin films are discussed in various national and international conferences where researchers interact through formal presentations and informal discussions, which in general do not give an opportunity for detailed analysis of the issues that are most critical for the advancement of the science of electroceramic thin films and devices. The field of research on electroceramic thin films and related devices has reached a state of development in which substantial progress has been made. However, there are some critical materials and device issues that need to be solved for the realization of commercially available devices.

The format of this NATO/ARW was designed to facilitate extensive scientific discussions. Key speakers reviewed the most relevant topics, making critical assessments of the current state of knowledge. Invited speakers presented recent advances on "hot" topics, and several participants presented papers related to new research. Each session concluded with extensive discussions in round table format, which permitted a fruitful and spirited interchange of ideas.

An important aspect of our NATO/ARW was that we were able to support the participation of several scientists from Eastern European Countries and contribute in this manner to the beginning of the new era of scientific cooperation between East and West promoted by NATO.

Orlando Auciello
North Carolina, 1994

Rainer Waser
Aachen, 1994

REPORT ON THE NATO/ARW

The NATO/ARW was divided in three sessions which included comprehensive reviews, invited papers on "hot" topics, contributed papers on new research, and extensive round table discussions following each session. In addition, a night session was dedicated to the discussion of highly speculative ideas. The three main subjects of the NATO/ARW in which this book is also organized are described below:

(1) Synthesis of ferroelectric thin films and their integration into heterostructures with metal and metal oxide electrodes. Presentations included characterization of films composition, microstructure, and electrical properties and their relationships. The discussions included consideration of various deposition techniques such as pulsed laser ablation deposition (PLAD), ion beam sputter-deposition (IBSD), metalorganic chemical vapor deposition (MOCVD), and sol-gel synthesis. Descriptions on the state of the art hardware and critical analyses of the basic principles of each thin film deposition technique were presented.

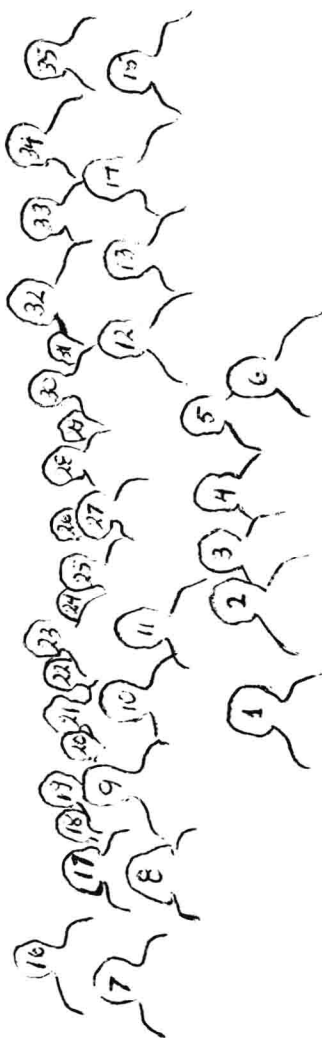
(2) Electrical characterization of ferroelectric capacitors and modeling, including pulse switching characterization of ferroelectric thin films, modeling of voltage dependent dielectric losses for ferroelectric MMIC devices, polarization, conduction, and breakdown in non-ferroelectric perovskite thin films, induced strain responses in ferroelectric, and relaxor ferroelectric and phase switching thin films. In addition, two comparatively new topics were discussed in this Session, namely, *in situ*, real-time analysis of ferroelectric/conductive oxide layers during growth by a new time-of-flight ion beam surface analysis technique, and electron emission from the surface of ferroelectric cathodes.

(3) Materials integration and application to devices, including discussions of ferroelectric thin films for sensor applications, integration of ferroelectric thin films for memory applications, fundamental properties and applications of sol-gel ceramic thin films, processing and device issues of high permittivity materials for DRAM memories, ferroelectric and piezoelectric devices: issues and potentials, and integrated ferroelectric microelectromechanical systems.

The NATO/ARW was attended by professionals, postdoctoral, and students from thirteen countries, including: Australia, Belgium, Canada, France, Germany, Italy, The Netherlands, Russia, Slovakia, Spain, Switzerland, United Kingdom, and The United States of America.

The main objective of the ARW was to bring together experts in the field of electroceramic thin films to discuss the status of the field and future directions in research and development. The highly interdisciplinary nature of the ARW allowed participants to interchange ideas in an environment rarely available in other international conferences.





33) G. Dietz, 34) Z. Sitar, 35) B.A. Tuttle,

25) L. Pardo, 26) J.F. Scott, 27) M.L. Calzada, 28) A.S. Sigov, 29) R.W. Whatmore,

30) G. Montesperelli, 31) H. Gundel, 32) J. Gerblinger,

16) P.K. Larsen, 17) M.I. Yanovskaya, 18) V. Craciun, 19) B.E. Gnade, 20) A.K. Tagantsev,

21) M. Kosec, 22) M. de Keijser, 23) D. Polla, 24) S.K. Dey,

7) P. Sutta, 8) M. Klee, 9) H. Achard, 10) D.J. Wouters, 11) G. Arlt, 12) D. Dimos,

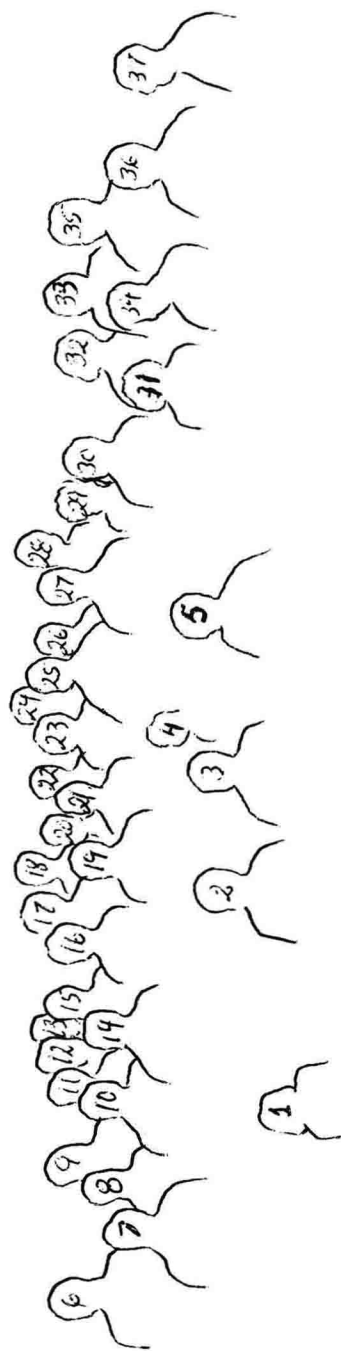
13) A.I. Kingon, 14) M. Sayer, 15) P. Kirby,

1) R. Waser, 2) S.B. Krupanidhi, 3) R. Ramesh, 4) H.N. Al-Shareef, 5) S.B. Desu, 6) O. Auciello

participants not present in the picture

L.E. Cross, P. Gaucher, A. Safari, D.M. Smyth





- 32) M.I. Yanovskaya, 33) P. Sutta, 34) L. Pardo, 35) M. Sayer, 36) G. Arlt, 37) A.K. Tagantsev,
 23) H. Gundel, 24) P. Gaucher, 25) H. Achard, 26) A.S. Sigov, 27) G. Dietz, 28) Z. Sitar,
 29) M. Kosec, 30) P. Kirby, 31) M.L. Calzada,
 15) D.J. Wouters, 16) J.F. Scott, 17) J. Gerblinger, 18) M. de Keijser, 19) S.B. Krupanidhi,
 20) H.N. Al-Shareef, 21) R.W. Whatmore, 22) S.B. Desu,
 6) P.K. Larsen, 7) R. Ramesh, 8) B.A. Tuttle, 9) D. Dimos, 10) V. Craciun, 11) G. Montesperelli,
 12) D.L. Polla, 13) B.E. Gnade, 14) A. Safari,
 1) M. Klee, 2) R. Waser, 3) O. Auciello, 4) Gundel, 5) A.I. Kingon

participants not present in the picture

L.E. Cross, S.K. Dey, D.M. Smyth

ACKNOWLEDGMENTS

The Directors of the NATO/ARW acknowledge the financial support of NATO, through the Scientific Affairs Division, the Advanced Research Projects Agency (USA), and the Office of Naval Research (USA). The directors are grateful to all program administrators and/or directors, and all the personnel in the Agencies mentioned above, who contributed with their work, in one way or another, to the success of this ARW. Last but not least, the Directors acknowledge the excellent organization of the Hotel Villa del Mare and its personnel, whom provided an excellent service and warm attention that contributed to the scientific and social success of the NATO/ARW.

TABLE OF CONTENTS

Preface	ix
Report on the NATO/ARW	xi
Acknowledgments	xvi
 PULSED LASER ABLATION-DEPOSITION AND CHARACTERIZATION OF FERROELECTRIC METAL OXIDE HETEROSTRUCTURES R. Ramesh, O. Auciello, V.G. Keramidas and R. Dat	 1
 LOW ENERGY ION BOMBARDMENT INDUCED EFFECTS IN MULTI-COMPONENT ELECTROCERAMIC THIN FILMS S.B. Krupanidhi	 23
 GROWTH AND PROPERTIES OF $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 AND $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ THIN FILMS BY PULSED LASER DEPOSITION A. Safari, C. Tantigate and J. Lee	 53
 WAVELENGTH DEPENDENCE IN PULSED LASER DEPOSITION OF ZnO THIN FILMS D. Craciun and V. Craciun	 67
 ORGANOMETALLIC CHEMICAL VAPOR DEPOSITION OF LEAD ZIRCONATE TITANATE M. de Keijser, P.J. van Veldhoven and G.J.M. Dormans	 75
 ALKOXIDE PRECURSORS FOR FERROELECTRIC THIN FILMS M.I. Yanovskaya, N.YA. Turova and L.I. Solov`Yova	 85
 DEPOSITION OF UNDOPED AND DOPED $\text{Pb}(\text{Mg},\text{Nb})\text{O}_3$ - PbTiO_3 , $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, ALKALINE EARTH TITANATE AND LAYERED PEROVSKITE THIN FILMS ON Pt AND CONDUCTIVE OXIDE ELECTRODES BY SPIN - ON PROCESSING: CORRELATION OF GROWTH AND ELECTRICAL PROPERTIES M. Klee, U. Mackens, J. Pankert, W. Brand and W. Klee	 99
 RELATIONSHIPS BETWEEN FERROELECTRIC 90° DOMAIN FORMATION AND ELECTRICAL PROPERTIES OF CHEMICALLY PREPARED $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ THIN FILMS B.A. Tuttle, T.J. Garino, J.A. Voigt, T.J. Headley, D. Dimos and M.O. Eatough	 117
 CHARACTERIZATION OF SOL-GEL $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ THIN FILM CAPACITORS WITH HYBRID (Pt, RuO_2) ELECTRODES H.N. Al-Shareef, O. Auciello and A.I. Kington	 133

ORGANICALLY MODIFIED SOL-GEL PRECURSORS FOR FERROELECTRIC DEPOSITION BY SPIN COATING P. Gaucher, J. Hector and J. C. Kurfiss	147
PREPARATION AND PROPERTIES OF CALCIUM MODIFIED LEAD TITANATE THIN FILMS M.L. Calzada, F. Carmona, R. Sirera and B. Jimenez	157
MICROSTRUCTURE OF LEAD TITANATE-BASED THIN FILMS L. Pardo, J. Ricote and M.L. Calzada	167
STOICHIOMETRY AND PHASE STRUCTURE OF SOL-GEL DERIVED PZT-BASED THIN FILMS M. Kosec, Y. Huang, E. Sato, A. Bell, N. Setter, G. Dražič, S. Bernik and T. Beltram	177
LIQUID PHASE EPITAXY OF $\text{Na}_{1-y}\text{K}_y\text{Ta}_{1-x}\text{Nb}_x\text{O}_3$ on KTaO_3 SUBSTRATES Z. Sitar, R. Gutmann and P. Günter	187
PULSE SWITCHING CHARACTERIZATION OF FERROELECTRIC THIN FILMS P.K. Larsen, R. Cuppens and G.J.M. Dormans	201
POLARIZATION, CONDUCTION, AND BREAKDOWN IN NON- FERROELECTRIC PEROVSKITE THIN FILMS R. Waser	223
ANOMALOUS LOGARITHMIC DEPENDENCIES IN D.C. BREAKDOWN OF FERROELECTRIC THIN FILMS J. F. Scott	249
THE SHAPE OF THE HYSTERESIS CURVE OF FERROELECTRIC SINGLE CRYSTALS AND CERAMICS G. Arlt	261
FAST TRANSIENT MEASUREMENTS ON ELECTROCERAMIC THIN FILMS G.W. Dietz, M. Schumacher and R. Waser	269
THE INFLUENCE OF DOPANTS ON THE LEAKAGE CURRENT IN PZT THIN-FILM FERROELECTRIC CAPACITORS D.J. Wouters, G. Willems, G. Groeseneken, H.E. Maes, K. Brooks and R. Klissurska	279
PHOTO-INDUCED STORAGE AND IMPRINTING IN $(\text{Pb,L a})(\text{Zr,Ti})\text{O}_3$ THIN FILMS D. Dimos, W. L. Warren and B. A. Tuttle	291

DEPLETION, DEPOLARIZING EFFECTS AND SWITCHING IN FERROELECTRIC THIN FILMS A.K. Tagantsev, M. Landivar, E. Colla, K. G. Brooks and N. Setter	301
NONSTOICHIOMETRY, DEFECTS, AND CHARGE TRANSPORT IN PZT M. V. Raymond and D. M. Smyth	315
X-RAY DIFFRACTION LINE PROFILE ANALYSIS OF ZnO THIN FILMS DEPOSITED ON Al-SiO ₂ -Si SUBSTRATES P. Sutta, Q. Jackuliak, V. Tvarozec and I. Novotny	327
ELECTRON EMISSION FROM FERROELECTRICS H. Gundel	335
INTEGRATION OF FERROELECTRIC THIN FILMS FOR MEMORY APPLICATIONS H. Achard and H. Mace	353
PROCESSING AND DEVICE ISSUES OF HIGH PERMITTIVITY MATERIALS FOR DRAMS B.E. Gnade, S.R. Summerfelt and D. Crenshaw	373
FERROELECTRIC THIN FILMS FOR CAPACITOR AND SENSOR APPLICATIONS R. W. Whatmore, P. Kirby, A. Patel, N. M. Shorrocks, T. Bland and M. Walker	383
PIEZOELECTRIC AND FERROELECTRIC DEVICES: POTENTIAL AND ISSUES M. Sayer, D.A. Barrow, R. Noteboom, E.M. Griswold and Z. Wu	399
INTEGRATED FERROELECTRIC MICROELECTROMECHANICAL SYSTEMS D. L. Polla	413
FUNDAMENTAL PROPERTIES AND SOME APPLICATIONS OF SOL-GEL CERAMIC THIN FILMS A.S. Sigov, V.I. Petrovsky, E.F. Pevtsov, K.A. Vorotilov and A.S. Valeev	427
SrTiO ₃ THIN FILMS FOR OXYGEN SENSORS J. Gerblinger and H. Meixner	439
INDEX	455

PULSED LASER ABLATION-DEPOSITION AND CHARACTERIZATION OF FERROELECTRIC METAL OXIDE HETEROSTRUCTURES

**R. RAMESH,¹ O. AUCIELLO,^{2,3}
V.G. KERAMIDAS¹ AND R. DAT³**

1. Bellcore, Red Bank, NJ 07701.

*2. MCNC, Electronics Technology Division
Research Triangle Park, NC 27709-2889,*

*3. N.C. State University, Department
of Materials Science and Engineering,
Raleigh, NC 27694-7179*

ABSTRACT. Materials integration strategies investigated by the NCSU-MCNC and Belcore groups have demonstrated that PZT-based heterostructure capacitors involving conductive oxide or hybrid metal-conductive oxide electrodes have negligible or no fatigue, long polarization retention and small tendency to imprint. The work reviewed involves the synthesis of heterostructure capacitors using the pulsed laser ablation deposition technique (PLAD). The properties observed for PZT-based heterostructure capacitors make them suitable for non-volatile ferroelectric memories. However, further work is necessary, particularly in producing small size capacitors ($\leq 1 \mu\text{m}^2$), to determine if scaling down to dimensions compatible with high density memories will introduce undesirable effects.

The work discussed shows that PLAD will remain a very useful technique for fundamental research, but extensive work is necessary to make it a viable method for device fabrication on large area substrates.

1. Introduction

1.1. BACKGROUND INFORMATION

There is currently a strong research and development effort directed at producing a commercially viable solid state, nonvolatile ferroelectric memory (FRAM) technology. Many laboratories are focusing their work on integrating sub-micron thin ferroelectric capacitors of, for example, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT), with the mature silicon based transistor technology to yield capacitor-transistor based memory architectures [1-5], as schematically illustrated in Fig.1. This figure also shows the perovskite unit cell of the ferroelectric PZT and the variety of interfaces (structural, chemical, electronic and ionic) that arise during the fabrication and integration of these metal oxide heterostructures on a Si substrate.