Defects in High- κ Gate Dielectric Stacks

NATO Science Series

A Series presenting the results of scientific meetings supported under the NATO Science Programme.

The Series is published by IOS Press, Amsterdam, and Springer in conjunction with the NATO Public Diplomacy Division

Sub-Series

I. Life and Behavioural Sciences	IOS Press
II. Mathematics, Physics and Chemistry	Springer
III. Computer and Systems Science	IOS Press
IV. Earth and Environmental Sciences	Springer

The NATO Science Series continues the series of books published formerly as the NATO ASI Series.

The NATO Science Programme offers support for collaboration in civil science between scientists of countries of the Euro-Atlantic Partnership Council. The types of scientific meeting generally supported are “Advanced Study Institutes” and “Advanced Research Workshops”, and the NATO Science Series collects together the results of these meetings. The meetings are co-organized by scientists from NATO countries and scientists from NATO’s Partner countries – countries of the CIS and Central and Eastern Europe.

Advanced Study Institutes are high-level tutorial courses offering in-depth study of latest advances in a field.

Advanced Research Workshops are expert meetings aimed at critical assessment of a field, and identification of directions for future action.

As a consequence of the restructuring of the NATO Science Programme in 1999, the NATO Science Series was re-organized to the four sub-series noted above. Please consult the following web sites for information on previous volumes published in the Series.

<http://www.nato.int/science>

<http://www.springer.com>

<http://www.iospress.nl>

Series II: Mathematics, Physics and Chemistry – Vol. 216

Defects in High- κ Gate Dielectric Stacks

Nano-Electronic Semiconductor Devices

edited by

Evgeni Gusev

IBM T.J. Watson Research Center,
New York, NY, U.S.A.

Published in cooperation with NATO Public Diplomacy Division

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

ISBN-10 1-4020-4366-X (PB)
ISBN-13 978-1-4020-4366-6 (PB)
ISBN-10 1-4020-4365-1 (HB)
ISBN-13 978-1-4020-4365-9 (HB)
ISBN-10 1-4020-4367-8 (e-book)
ISBN-13 978-1-4020-4367-3 (e-book)

Published by Springer,
P.O. Box 17, 3300 AA Dordrecht, The Netherlands.

www.springer.com

Printed on acid-free paper

All Rights Reserved

© 2006 Springer

No part of this work 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, with the exception of any material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work.

Printed in the Netherlands.

TABLE OF CONTENTS

Preface	ix
HIGH-K TECHNOLOGY	
PVD High-k Gate Dielectrics with FUSI Gate and Influence of PDA Treatment on On-state Drive Current <i>M. Niwa, R. Mitsuhashi, K. Yamamoto, S. Hayashi, A. Rothchild, S. Kubicek, S. De Gendt, S. Biesemans</i>	1
Extremely High-Density Capacitors with ALD High-k Dielectric Layers <i>J. Klotwijk, A. Kemmeren, R. Wolters, F. Roozeboom, J. Verhoeven, E. Van Den Heuvel</i>	17
Towards Understanding of Processing-nanostructure-property Inter-relationships in High-k/Metal Gate Stacks <i>P. Majhi, G. Bersuker, B. H. Lee</i>	29
DEFECTS IN HIGH-K DIELECTRICS: CHARACTERIZATION	
On the Characterization of Electronically Active Defects in High-k Gate Dielectrics <i>D.A. Buchanan, D. Felnhofer</i>	41
Inelastic Electron Tunneling Spectroscopy (IETS) Study of High-k Dielectrics <i>T.P. Ma, W. He, M. Wang</i>	61
Characterization and Modeling of Defects in High-k Layers Through Fast Electrical Transient Measurements <i>J. Mitard, C. Leroux, G. Reimbold, X. Garros, F. Martin, G. Ghibaudo</i>	73
Characterization of Electrically Active Defects in High-k Gate Dielectrics Using Charge Pumping <i>E. M. Vogel, D. W. Heh</i>	85
Impact of High-k Properties on MOSFET Electrical Characteristics <i>L. Pantisano, L.-Å. Ragnarsson, M. Houssa, R. Degraeve, G. Groeseneken, T. Schram, S. Degendt, M. Heyns, V. Afanas'ev</i>	97
HIGH-K PROCESSING AND DEFECTS	
Structural Evolution and Point Defects in Metal Oxide-based High-k Gate Dielectrics <i>P. C. McIntyre, H. Kim, K. C. Saraswat</i>	109

Disordered Structure and Density of Gap States in High-Permittivity Thin Solid Films	123
<i>K. Kukli, S. Dueñas, H. Castán, H. García, J. Barbolla, J. Aarik, A. Aidla, M. Ritala, M. Leskelä</i>	
Interdiffusion Studies of High-k Gate Dielectric Stack Constitutes	135
<i>P. Sivasubramiani, M. A. Quevedo-Lopez, T.H. Lee, M.J. Kim, B.E. Gnade, R. M. Wallace</i>	
XPS/LEIS Study of High-k Rare Earth (Lu, Yb) Oxides and Silicates on Si: The Effect of Annealing on Microstructure Evolution	147
<i>A. Zenkevich, Y. Lebedinskii, G. Scarel, M. Fanciulli</i>	
Transient Charging Effects and Its Implications to The Reliability of High-k Dielectrics	161
<i>B. H. Lee, R. Choi, R. Harris, S.A. Krishan, C. D. Young, J. Sim, G. Bersuker</i>	
HIGH-K THEORY	
Defect Energy Levels in High-k Gate Oxides	175
<i>J. Robertson, K. Xiong, S. J. Clark</i>	
Defect-related Issues in High-k Dielectrics	189
<i>S. T. Pantelides, M. H. Evans, D. M. Fleetwood, E. P. Gusev, J. D. Joannopoulos, Z. Lu, S. J. Pennycook, S. N. Rashkeev, R. D. Schrimpf, L. Tsetseris, K. Van Benthem, X-G. Zhang, X. J. Zhou</i>	
Studying The Effects of Nitrogen and Hafnium Incorporation into The SiO ₂ /Si(100) Interface with Replica-exchange Molecular Dynamics and Density-Functional-Theory Calculations	203
<i>W. Andreoni, A. Curioni, D. Fischer, S. R. Billeter, C. A. Pignedoli</i>	
ELECTRICALLY ACTIVE DEFECTS	
Probing Point Defects and Traps in Stacks of Ultrathin Hafnium Oxides on (100)Si by Electron Spin Resonance: Interfaces and N Incorporation	215
<i>A. Stesmans, V. V. Afanas'ev</i>	
Mechanism of Charge Trapping Reduction in Scaled High-k Gate Stacks	227
<i>G. Bersuker, B. H. Lee, H. R. Huff, J. Gavartin, A. Shluger</i>	

TABLE OF CONTENTS

vii

Electrically Active Interface and Bulk Semiconductor Defects in High-k / Germanium Structures <i>A. Dimoulas</i>	237
Defect and Composition Analysis of as-deposited and Nitrided (100)Si / SiO ₂ / Hf _{1-x} Si _x O ₂ Stacks by Electron Paramagnetic Resonance and Ion Beam Analysis <i>H. J. von Bardeleben, J. L. Cantin, J. J. Ganem, I. Trimaille, E. P. Gusev</i>	249
Defects at the High-k /Semiconductor Interfaces Investigated by Spin Dependent Spectroscopies <i>M. Fanciulli, O. Costa, S. Baldovino, S. Cocco, G. Seguini, E. Prati, G. Scarel</i>	263
Fixed Oxide Charge in Ru-based Chemical Vapour Deposited High-k Gate Stacks <i>K. Frohlich, R. Lupták, M. Ľapajna, K. Hušeková, U. Weber, P.K. Baumann, J. Lindner</i>	277
Electrical Defects in Atomic Layer Deposited HfO ₂ Films on Silicon: Influence of Precursor Chemistries and Substrate Treatment <i>S. Dueñas, H. Castán, H. García, L. Bailón, K. Kukli, M. Ritala, M. Leskelä</i>	287
The Effects of Radiation and Charge Trapping on The Reliability of Alternative Gate Dielectrics <i>J. A. Felix, M. R. Shaneyfelt, J. R. Schwank, P. E. Dodd, D. M. Fleetwood, X. J. Zhou, E. P. Gusev</i>	299
Can LEIS Spectra Contain Information on Surface Electronic Structure of High-k Dielectrics <i>Y. Lebedinskii, A. Zenkevich, M. Pushkin, N. Barantsev, V. Troyan, V. Nevolin</i>	323
Low Substrate Damage High-k Removal After Gate Patterning <i>D. Shamiryan, V. Paraschiv, M. Claes, W. Boullart</i>	331
Monitoring of Fermi Level Variations at Metal/High-k Interfaces with <i>in situ</i> X-ray Photoelectron Spectroscopy <i>Y. Lebedinskii, A. Zenkevich, E. P. Gusev</i>	339

INTERFACES

Structure, Composition and Order at Interfaces of Crystalline Oxides and Other High-k Materials on Silicon <i>T. Gustafsson, E. Garfunkel, L. Goncharova, D. Starodub, R. Barnes, M. Dalponte, G. Bersuker, B. Foran, P. Lysaght, D. G. Schlom, V. Vaithyanathan, M. Hong, J. R. Kwo</i>	349
---	-----

Interface Formation During Epitaxial Growth of Binary Metal Oxides on Silicon	361
<i>H. J. Osten, A. Fissel, O. Kirfel, Z. Elassar, E. Bugiel, M. Czernohorsky</i>	
Effect of Chemical Environment and Strain on Oxygen Vacancy Formation Energies at Silicon-Silicon Oxide Interfaces	373
<i>T.M. Henderson, J.C. Greer, G. Bersuker, A. Korkin, R.J. Bartlett</i>	
Dielectric and Infrared Properties of Ultrathin SiO ₂ Layers on Si (100)	385
<i>F. Giustino, A. Pasquarello</i>	
The (100) Surface of Semiconductor Silicon (in Practical Conditions): Preparation, Evolution, Passivation	397
<i>G.F. Cerofolini</i>	
PROCESSING, CHARACTERIZATION AND DEVICES	
Correlation Between Defects, Leakage Currents and Conduction Mechanisms in Thin High-k Dielectric Layers	411
<i>A. Paskaleva, E. Atanassova, M. Lemberger, A. J. Bauer</i>	
Electronic Structure of ZrO ₂ and HfO ₂	423
<i>T. V. Perevalov, A. V. Shaposhnikov, K.A. Nasyrov, D. V. Gritsenko, V. A. Gritsenko, V. M. Tapilin</i>	
High-k Gate Stacks Electrical Characterization at the Nanoscale using Conductive-AFM	435
<i>M. Nafria, X. Blasco, M. Porti, L. Aguilera, X. Aymerich</i>	
Magnetic Defects in Pristine and Hydrogen-Terminated Nanodiamonds	447
<i>V. Osipov, M. Baidakova, K. Takai, T. Enoki, A. Vul'</i>	
On the Importance of Atomic Packing in Determining Dielectric Permittivities	457
<i>A. H. Edwards, T. Busani, R. A. B. Devine, A. Pineda</i>	
Investigation of The Electronic Properties of Thin Dielectric Films by Scanning Probe Microscopy	471
<i>D.A. Antonov, D.O. Filatov, A.V. Kruglov, G.A. Maximov, A. V. Zenkevich, Y. Lebedinskii</i>	
Subject Index	481
Author Index	485
List of Workshop Participants	489

PREFACE

The goal of this NATO Advanced Research Workshop (ARW) entitled “Defects in Advanced High-k Dielectric Nano-electronic Semiconductor Devices”, which was held in St. Petersburg, Russia, from July 11 to 14, 2005, was to examine the very complex scientific issues that pertain to the use of advanced high dielectric constant (high-k) materials in next generation semiconductor devices. The special feature of this workshop was **focus on** an important issue of **defects** in this novel class of materials.

One of the key obstacles to high-k integration into Si nano-technology are the electronic defects in high-k materials. It has been established that defects do exist in high-k dielectrics and they play an important role in device operation. However, very little is known about the nature of the defects or about possible techniques to eliminate, or at least minimize them. Given the absence of a feasible alternative in the near future, well-focused scientific research and aggressive development programs on high-k gate dielectrics and related devices must continue for semiconductor electronics to remain a competitive income producing force in the global market.

To progress towards overcoming the many fundamental obstacles blocking integration of high-k dielectrics into nano-semiconductor technology and to improve our basic knowledge of these emerging materials, more than 60 leading researchers from 16 countries around the globe gathered together at this workshop to share their recent results and thinking and to establish new collaborations with the ultimate goal to develop an atomic-scale understanding of defects in high-k and their role in devices. During this 4-day ARW, NATO country and “Eastern Block” based scientists met, tutored each other and defined directions as to where research and development should be focused over the next five years. Many of the speakers were from Europe, the U.S. and Canada. Several key speakers came from leading centers in the former USSR (Moscow, Novosibirsk, and St. Petersburg). The list of researchers represented a rather diverse group of scientists and engineers from academic, industrial and governmental labs, and included both experimental and theoretical researchers with backgrounds in basic and applied areas of physics, chemistry, electrical engineering, surface science, and materials science.

Following several introductory presentations, the first day was concentrate on processing and physical and structural properties of high-k materials (HfO_2 , ZrO_2 , Al_2O_3 , Y_2O_3 , silicates, etc) . A thorough knowledge of bulk materials properties and interfaces is required before these complex multi-component systems can hope to be understood or optimized. It was followed by a discussion of experimental and theoretical investigations of defects. The

focus of the 3rd day was electrical characterization, defects structure and effect on device performance. This day was concluded by a poster session, giving special priority to younger researchers to present and discuss their work. Finally, a review and open discussion was held to focus on both individual and collective plans for future research on defects in high-K dielectrics.

The enjoyment of the week came not only from the excellent presentations and stimulating discussions, but from the beauty of St. Petersburg amplified by gorgeous summer weather. The foreigners among us were not only delighted in the “physical” beauty of the city (architecture, Neva-river, canals, palaces, parks, etc.) but enjoyed rich cultural experiences (the Hermitage, the Palaces, opera, ballet) and the hospitality of local people.

The editor would like to thank the co-Director, Dr. V. Osipov, and the members of the International Advisory Committee, Prof. D. Buchanan, Dr. A. Dimoulas, Dr. A. Edwards, Prof. E. Garfunkel, and Prof. J. Robertson, for help in selecting participants from different countries and for their valuable comments on the scientific program. I would also like to thank all invited speakers and contributors to this book for their support and encouragement during the early planning stages of the Workshop and cooperation in meeting publication deadline. The success of the Workshop would not have been possible without the excellent planning and operation of the local team in St. Petersburg led by Dr. S. Kidalov and I. Vorobieva. It was a real pleasure to collaborate with this professional team again, after another successful NATO ARW on “Fundamental Aspects of Ultrathin Dielectrics on Si-based Devices: Towards an Atomic-scale Understanding” in 1997. I am very grateful to Dr. V. Siklitsky for developing and maintaining the website (<http://www.ioffe.ru/natoarw/2005/>) and also for his help during the Workshop. I am thankful to all participants for their high-quality presentations, active participation (including peer-reviewing papers presented in this book) and fruitful discussions at the Workshop. Finally and importantly, I would like to acknowledge the hard editorial work of O. Elyukhina and D. Solnyshkov who helped us to put together presented papers into this book. The Workshop would not have been possible without financial support from the NATO Public Diplomacy Division. We also greatly appreciate financial contributions from co-sponsors, the Russian Foundation for Basic Research, the U.S. National Science Foundation (NSF), the European Office of Aerospace Research and Development (EOARD), and International SEMATECH.

August 2005
Saratoga, California

Evgeni Gusev