

1 JANUARY 2000

VOLUME 87 NUMBER 1

530.5
py

PHYSICS-ASTRONOMY

JAN 0 5 2000
LIBRARY

JOURNAL OF APPLIED PHYSICS

PHYSICS

UNIVERSITY OF WASHINGTON

JAN 05 2000

LIBRARIES

AMERICAN
INSTITUTE
OF PHYSICS

AVAILABLE ONLINE—See <http://ojps.aip.org/japo/>

MICRON Ex.1070.00001

Micron v. Harvard, IPR2017-00664

JOURNAL OF APPLIED PHYSICS

CODEN: JAPIAU

ISSN: 0021-8979

URL: <http://ojps.aip.org/japo/>

Editor

Steven J. Rothman
Argonne National Laboratory, Argonne, IL

Associate Editors

Roy Benedek
Robert C. Birtcher
Gian P. Felcher
Mitio Inokuti
Simon R. Phillpot

Editor, Applied Physics Reviews

John M. Poate
New Jersey Institute of Technology, Newark, NJ

Editorial Board

Term ending 31 December 2000

Robert Hull (University of Virginia, Charlottesville, VA)
Georges Martin (Commissariat à l'Energie Atomique, Saclay)
Jerry R. Meyer (Naval Research Laboratory, Washington, DC)

Term ending 31 December 2001

Shuji Nakamura (Nichia Chemical Ind., Ltd., Tokushima)
R. Ramesh (University of Maryland, College Park, MD)
Frans Spaepen (Harvard University, Cambridge, MA)

Term ending 31 December 2002

Dana D. Dlott (University of Illinois, Urbana, IL)
Franz Faupel (Universität Kiel, Kiel, Germany)
Karen L. Kavanagh (Univ. of California, San Diego, La Jolla, CA)
John P. Wikswo (Vanderbilt University, Nashville, TN)

Editorial Office Staff

Diane M. Kurtz, *Editorial Supervisor*; Catherine M. Dial, *Editorial Assistant*; Lucila Morales, Bonnie S. Peters, Suzanne C. Marik, Leslie A. Weltmeyer, Lori A. Randolph, Arlene J. Niemann, *Editorial Support*

Information for Authors

Submissions: Submit manuscripts (3 copies) to Editor, *Journal of Applied Physics*, Argonne National Laboratory, Building 203, Room R-127, P.O. Box 8296, 9700 South Cass Avenue, Argonne, IL 60439-4871 (E-mail: jap@anl.gov). Submission implies that the manuscript has not been published previously, and is not currently submitted for publication elsewhere. For detailed information for contributors, visit the above URL.

Publication Charge: To support the cost of wide dissemination of research results through publication of journal pages and production of a database of articles, the author's institution is requested to pay a page charge of \$60 per page (with a one-page minimum) and an article charge of \$20 per article. For Errata the minimum page charge is \$10, with no article charge. For any regular, published article that exceeds 10 journal pages, a mandatory \$150 page charge will be added for each page in excess of 10 pages.

Reprints: Authors may order reprints with or without covers only in multiples of 50 (with a minimum of 100 in each category) from AIP, Circulation & Fulfillment/Reprints, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502; Fax: 631-576-2230; Telephone: 800-344-6909 (U.S. and Canada), or 631-576-2230.

Electronic Physics Auxiliary Publication Service (EPAPS): EPAPS is a low-cost electronic depository for material that is supplemental to a journal article. For a nominal fee, authors may submit multimedia (e.g., movie files, audio files, 3D rendering files), color figures, data tables, etc. Retrieval instructions are footnoted in the related published paper. Prominent links in the online journal article allow users to navigate directly to the associated EPAPS deposit. Direct requests to the Editor; for additional information see <http://www.aip.org/pub/servs/epaps.html>.

Comments: Authors may direct comments on the journal or on the editorial process to Dorene Berger, Manager, Editorial Operations, AIP, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502. Telephone: 631-576-2444; Fax: 631-576-2450; E-mail: dberger@aip.org.

Journal of Applied Physics (AIP) archival material for significant new results in applied physics; there are two issues per month. The journal publishes articles that emphasize understanding of the physics underlying modern technology, but distinguished from technology on the one side and pure physics on the other. *Applied Physics Reviews* is a series of occasional review articles on topics within this scope. The Proceedings of the Conference on Magnetism and Magnetic Materials is an annual feature.

AIP Production: Deborah McHone, *Editorial Supervisor*; Margaret Reilly, *Journal Coordinator*; Janet Panarelli, *Chief Production Editor*; Marilyn Schrage, *Senior Production Editor*; Cathleen Nelson, *Production Editor*

Prices

2000 Subscriptions

	U.S.A. & Poss.	Can., Mex., Central & S. Amer. & Caribbean ^a	Europe, Asia, Middle East, Africa & Oceania	
			Surface	Air Freight
Member^b				
Print + online ^c	\$255 ^d	\$360	\$360	\$525
Quarterly CD-ROM + online	\$255	\$255	\$255	\$255
Online only ^c	\$155	\$155	\$155	\$155
Nonmember				
Print + online ^c	\$2,855 ^d	\$2,960	—	\$3,125
Quarterly CD-ROM + online	\$2,855	\$2,855	—	\$2,855
Online only ^c	\$2,285	\$2,285	—	\$2,285

^aThese are Surface Mail subscription rates. Surface Mail rates apply to Canada and Mexico, to countries not served by air freight, and to Member Subscribers not electing optional air freight.

^bAIP Member and Affiliated Societies.

^cAnnual CD-ROM (2 discs) is an additional \$30 for members and \$50 for nonmembers.

^dRate also applies to Microfiche+online, to all destinations.

Back Issues: 2000 single copies: \$130. Prior to 2000 single copies: \$30 for members; \$120 for nonmembers.

Additional Availability

Online Access: The *Journal of Applied Physics* is available online; for details, please see <http://ojps.aip.org/japo/>. Abstracts of journal articles are available from AIP's SPIN Web Service (<http://ojps.aip.org/spinweb/>).

Microform: The *Journal of Applied Physics* is available on microfiche issued at the same frequency as the printed journal, and annually on microfilm. Direct requests to AIP, Circulation & Fulfillment/Single Copy Sales, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502; Fax: 631-349-9704; Telephone: 800-344-6908 (U.S. and Canada) or 631-576-2230.

Document Delivery: Copies of journal articles can be ordered for online delivery from the Articles in Physics online document delivery service (<http://ojps.aip.org/jhtml/artinphys/>).

Customer Service

Subscription Orders and Renewals should be addressed to American Institute of Physics, P.O. Box 503284, St. Louis, MO 63150-3284. Telephone: 800-344-6902 (U.S. and Canada) or 631-576-2230; Fax: 631-349-9704; E-mail: subs@aip.org. Allow at least six weeks advance notice.

Inquiries, Address Changes, Claims, Single Copy Replacements, and Back Volumes:

For address changes, please send both old and new addresses and, if possible, include the mailing label from a recent issue. Missing issue requests will be honored only if received within six months of publication date (nine months for Australia and Asia). Single copies of a journal may be ordered and back volumes are available in print, microfiche, or microfilm. Contact AIP Customer Services at 800-344-6902 (U.S. and Canada) or 631-576-2230; Fax: 631-349-9704; E-mail: subs@aip.org.

Reprint Billing: Contact AIP Publication Charge and Reprints/CFD, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502; Telephone: 800-344-6909 (U.S. and Canada) or 631-576-2230; E-mail: pcr@aip.org.

Rights and Permissions

Copying: Single copies of individual articles may be made for private use or research. Authorization is given (as indicated by the Item Fee Code for this publication) to copy articles beyond the use permitted by Sections 107 and 108 of the U.S. Copyright Law, provided the copying fee of \$17 per copy per article is paid to the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, USA. Persons desiring to photocopy materials for classroom use should contact the CCC Academic Permissions Service. The Item Fee Code for this publication is 0021-8979/2000 \$17.00.

Authorization does not extend to systematic or multiple reproduction, to copying for promotional purposes, to electronic storage or distribution, or to republication in any form. In all such cases, specific written permission from AIP must be obtained.

Other Use: Permission is granted to quote from the journal with the customary acknowledgment of the source. To reprint a figure, table, or other excerpt requires the consent of one of the authors and notification to AIP.

Requests for Permission: Address requests to AIP Office of Rights and Permissions, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502; Fax: 631-576-2450; Telephone: 631-576-2268; E-mail: rights@aip.org.

Journal of Applied Physics (ISSN: 0021-8979) is published semimonthly by the American Institute of Physics. 2000 subscription rates are: US\$2855. POSTMASTER: Send address changes to *Journal of Applied Physics*, Suite 1N01, 2 Huntington Quadrangle, Melville, NY 11747-4502. Periodicals postage paid at Huntington Station, NY, 11746, and additional mailing offices.

Copyright © 2000 American Institute of Physics. All rights reserved.

MICRON Ex.1070.00002

Micron v. Harvard, IPR2017-00664

JOURNAL OF APPLIED PHYSICS

Volume 87

January – June 2000

Editor

Steven J. Rothman

Associate Editors

Roy Benedek
Robert C. Birtcher

Gian P. Felcher
Mitio Inokuti

Simon R. Phillpot

Assistant to the Editor

Catherine M. Dial

Editorial Board

Robert Hull
Georges Martin
Jerry R. Meyer

Shuji Nakamura
R. Ramesh
Frans Spaepen

Dana D. Dlott
Franz Faupel
Karen L. Kavanagh
John P. Wikswo

a publication of the American Institute of Physics

AIP

MICRON Ex.1070.00003

Micron v. Harvard, IPR2017-00664

viii EDITORIAL: Editorial Policies

x INFORMATION FOR CONTRIBUTORS

LASERS, OPTICS, AND OPTOELECTRONICS (PACS 42)

- 1 Series resistance and its effect on the maximum output power of $1.5\text{ }\mu\text{m}$ strained-layer multiple-quantum-well ridge waveguide InGaAsP lasers
- 5 Finite-cell-gap corrections to the capacitance analysis of liquid crystal displays with periodic interdigital electrodes
- 10 A scalar variational method for resonant modes of oxide-apertured vertical-cavity surface-emitting lasers
- 22 Optical second-harmonic generation in lead formate
- 25 $\text{Co}^{2+}:\text{ZnS}$ and $\text{Co}^{2+}:\text{ZnSe}$ saturable absorber Q switches

B. B. Elenkrig, S. Smetona, J. G. Simmons, B. Takasaki, J. D. Evans, T. Makino

C.-J. Chen

K. Y. Chang, J. Woodhead, J. Roberts, P. N. Robson

K. Betzler, H. Hesse, R. Jaquet, D. Lammers

Tzong-Yow Tsai, Milton Birnbaum

PLASMAS AND ELECTRICAL DISCHARGES (PACS 51–52)

- 30 The transmittance pattern in a mesoscopic nonuniform necklace like system

Hon-Lung Mak, Hai-Qing Lin, Zhiwen Pan, Chang-De Gong

STRUCTURAL, MECHANICAL, THERMODYNAMIC, AND OPTICAL PROPERTIES OF CONDENSED MATTER (PACS 61–68, 78)

- 36 Excimer laser-induced temperature field in melting and resolidification of silicon thin films
- 44 Scanning tunneling microscopy and spectroscopy characterization of ion-beam-induced dielectric degradation in ultrathin SiO_2 films and its thermal recovery process
- 49 Production of amorphous zones in GaAs by the direct impact of energetic heavy ions
- 57 Dwell-time related effects in focused ion beam synthesis of cobalt disilicide
- 63 Elastic properties of nanoparticle chain aggregates of TiO_2 , Al_2O_3 , and Fe_2O_3 generated by laser ablation
- 74 Spatial and angle distribution of internal stresses in nano- and microstructured chemical vapor deposited diamond as revealed by Brillouin spectroscopy
- 78 Phase formation due to high dose aluminum implantation into silicon carbide
- 86 Electromigration-induced drift in damascene and plasma-etched Al(Cu). I. Kinetics of Cu depletion in polycrystalline interconnects
- 99 Electromigration-induced drift in damascene and plasma-etched Al(Cu). II. Mass transport mechanisms in bamboo interconnects
- 110 Deuterium diffusion through hexagonal boron nitride thin films
- 117 Zinc self-diffusion, electrical properties, and defect structure of undoped, single crystal zinc oxide
- 124 Effects of precursors and substrate materials on microstructure, dielectric properties, and step coverage of $(\text{Ba}, \text{Sr})\text{TiO}_3$ films grown by metalorganic chemical vapor deposition

Mutsuko Hatano, Seungjae Moon, Minghong Lee, Kenkichi Suzuki, Costas P. Grigoropoulos

Heiji Watanabe, Toshio Baba, Masakazu Ichikawa

M. W. Bench, I. M. Robertson, M. A. Kirk, I. Jencić

Stephan Hausmann, Lothar Bischoff, Jochen Teichert, Matthias Voelskow, Wolfhard Möller

K. Ogawa, T. Vogt, M. Ullmann, S. Johnson, S. K. Friedlander

J. K. Krüger, J. P. Embs, S. Lukas, U. Hartmann, C. J. Brierley, C. M. Beck, R. Jiménez, P. Alnot, O. Durand

V. Heera, H. Reuther, J. Stoemenos, B. Péc

Joris Proost, Ann Witvrouw, Karen Maex, Jan D'Haen, Patrick Cosemans

Joris Proost, Karen Maex, Luc Delacy

Riccardo Checchetto, Antonio Miotello

Gregory W. Tomlins, Jules L. Routbort, Thomas O. Mason

Y. Gao, S. He, P. Alluri, M. Engelhard, A. S. Lea, J. Finder, B. Melnick, R. L. Hance

(Continued)

- 133 Structural characterization of oxidized allotaxially grown CoSi_2 layers by x-ray scattering
 - 140 Influence of surface topography on depth profiles obtained by Rutherford backscattering spectrometry
 - 144 Relative importance of the Si-Si bond and Si-H bond for the stability of amorphous silicon thin film transistors
 - 155 Temperature effect on a rubbed polyimide alignment layer
 - 159 Stranski-Krastanov growth of Al on Cr layers during molecular-beam epitaxial growth and its influence on the structure of epitaxial (001) Al/Cr superlattices
 - 168 Texture of Al thin films deposited by magnetron sputtering onto epitaxial W(001)
 - 172 Al concentration control of epitaxial AlGaIn alloys and interface control of GaN/AlGaIn quantum well structures
 - 177 Residual stress, microstructure, and structure of tungsten thin films deposited by magnetron sputtering
 - 188 Influence of indium composition on the surface morphology of self-organized $\text{In}_x\text{Ga}_{1-x}\text{As}$ quantum dots on GaAs substrates
 - 192 Structural characterization of rapid thermal oxidized $\text{Si}_{1-x-y}\text{Ge}_x\text{C}_y$ alloy films grown by rapid thermal chemical vapor deposition
 - 198 The electro-optical behavior of SrS:Ce electroluminescent devices under photonic excitation
 - 203 Photoluminescence properties of Zn-doped heterostructures having native-oxide layers
 - 207 Photostimulated luminescence process in the x-ray storage phosphor CsBr:Ga^{+}
 - 212 Nonlinear optical properties of Cu_xS and CuInS_2 nanoparticles in sol-gel glasses
 - 217 Pockels effect in photopolymers derived from ferroelectric liquid crystals
 - 223 Photocapacitive detection of hole emission from DX center in *n*-type $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ doped with Te
 - 228 Spectroellipsometric characterization of plasma-deposited Au/SiO₂ nanocomposite films
 - 236 Thermoluminescence in ZnO doped ZrO₂ induced by 2.5–9 keV x-ray synchrotron radiation
 - 241 Energy-level engineering of self-assembled quantum dots by using AlGaAs alloy cladding layers
 - 245 Effects of rapid thermal annealing on the optical properties of $\text{GaIn}_x\text{As}_{1-x}/\text{GaAs}$ single quantum well structure grown by molecular beam epitaxy
- I. D. Kaendler, O. H. Seeck, J.-P. Schlomka, M. Tolan, W. Press, J. Stettner, L. Kappius, C. Dieker, S. Mantl
- J. Slotte, A. Laakso, T. Ahlgren, E. Rauhala, R. Salonen, J. Räisänen, A. Simon, I. Uzonyi, A. Z. Kiss, E. Somorjai
- R. B. Wehrspohn, S. C. Deane, I. D. French, I. Gale, J. Hewett, M. J. Powell, J. Robertson
- Jong-Hyun Kim, Charles Rosenblatt
- Toshiki Kingetsu, Yasuhiro Kamada, Masahiko Yamamoto
- Lynnette D. Madsen, Erik B. Svedberg, Daniel B. Bergstrom, Ivan Petrov, Joseph E. Greene
- Sung Chul Choi, Jong-Hee Kim, Ji Youn Choi, Kang Jae Lee, Kee Young Lim, Gye Mo Yang
- Y. G. Shen, Y. W. Mai, Q. C. Zhang, D. R. McKenzie, W. D. McFall, W. E. McBride
- Hanxuan Li, Qiangdong Zhuang, Zhanguo Wang, Theda Daniels-Race
- W. K. Choi, J. H. Chen, L. K. Bera, W. Feng, K. L. Pey, J. Mi, C. Y. Yang, A. Ramam, S. J. Chua, J. S. Pan, A. T. S. Wee, R. Liu
- J. Benoit, C. Barthou, P. Benalloul, K. Polamo
- B. P. Tinkham, R. D. Dupuis
- U. Rogulis, S. Schweizer, S. Assmann, J.-M. Spaeth
- A. M. Malyarevich, K. V. Yumashev, N. N. Posnov, V. P. Mikhailov, V. S. Gurin, V. B. Prokopenko, A. A. Alexeenko, I. M. Melnichenko
- N. Pereda, J. Etxebarria, C. L. Folcia, J. Ortega, C. Artal, M. B. Ros, J. L. Serrano
- Akihiko Murai, Yutaka Oyama, Jun-ichi Nishizawa
- Dan Dalacu, Ludvik Martinu
- Lee-Jene La, Ching-Shen Su
- Y. S. Kim, U. H. Lee, D. Lee, S. J. Rhee, Y. A. Leem, H. S. Ko, D. H. Kim, J. C. Woo
- L. H. Li, Z. Pan, W. Zhang, Y. W. Lin, Z. Q. Zhou, R. H. Wu



(Continued)

- 249 Photoionization of deep centers in Al_2O_3
- 257 Lack of proportionality of total electron yield and soft x-ray absorption coefficient
- 269 Raman spectra and laser properties of Yb-doped yttrium orthovanadate crystals
- 274 Polarized photoluminescence and order parameters of "in situ" photopolymerized liquid crystal films
- 280 Piezoreflectance study of an Fe-containing silicon carbon nitride crystalline film
- Von H. Whitley, S. W. S. McKeever
H. Henneken, F. Scholze, G. Ulm
- H. R. Xia, L. X. Li, H. J. Zhang,
X. L. Meng, L. Zhu, Z. H. Yang,
X. S. Liu, J. Y. Wang
- C. Sánchez, B. Villacampa, R.
Cases, R. Alcalá, C. Martínez, L.
Oriol, M. Piñol
- C. H. Hsieh, Y. S. Huang, K. K.
Tiong, C. W. Fan, Y. F. Chen, L. C.
Chen, J. J. Wu, K. H. Chen

ELECTRONIC STRUCTURE AND TRANSPORT (PACS 71-73)

- 285 Abnormal temperature dependence of band-gap energies observed in (InAs)/(GaAs) and (InP)/(GaP) superlattices with strong lateral composition modulation
- 289 Valence band photoemission, band bending, and ionization energy of GaAs(100) treated in alcoholic sulfide solution
- 295 Dependence of indium-tin-oxide work function on surface cleaning method as studied by ultraviolet and x-ray photoemission spectroscopies
- 299 Magnetoresistance of constricted ferromagnetic wires
- 303 Improved algorithm for modeling collision broadening through a sequence of scattering events in semiclassical Monte Carlo
- 312 Charge transport in a blue-emitting alternating block copolymer with a small spacer to conjugated segment length ratio
- 317 Thermoelectric properties of pure and doped FeMSb ($M=\text{V}, \text{Nb}$)
- 322 Time-resolved photocurrent and electric field measurements in high resistivity CdTe
- 329 Monte Carlo method for the investigation of electron diffusion in degenerate semiconductors
- 334 Two dimensional electron gases induced by spontaneous and piezoelectric polarization in undoped and doped AlGaIn/GaN heterostructures
- 345 Temperature behavior of multiple tunnel junction devices based on disordered dot arrays
- 353 Comparison of zinc-blende and wurtzite GaN semiconductors with spontaneous polarization and piezoelectric field effects
- 365 Microstructure and electrical resistivity of Cu and Cu_3Ge thin films on $\text{Si}_{1-x}\text{Ge}_x$ alloy layers
- 369 Characterization of an AlGaIn/GaN two-dimensional electron gas structure
- Shu-Tsun Chou
- Mikhail V. Lebedev, Masakazu Aono
- Kiyoshi Sugiyama, Hisao Ishii, Yukio Ouchi, Kazuhiko Seki
- A. O. Adeyeye, R. P. Cowburn, M. E. Welland
- Leonard F. Register, Karl Hess
- Dongge Ma, I. A. Hümmelgen, Xiabin Jing, Zhiyong Hong, Lixiang Wang, Xiaojiang Zhao, Fosong Wang, F. E. Karasz
- D. P. Young, P. Khalifah, R. J. Cava, A. P. Ramirez
- G. Ghislotti, S. Pietralunga, L. Ripamonti, R. Sacco, S. Micheletti, F. Bosisio
- P. Borowik, J. L. Thobel
- O. Ambacher, B. Foutz, J. Smart, J. R. Shealy, N. G. Weimann, K. Chu, M. Murphy, A. J. Sierakowski, W. J. Schaff, L. F. Eastman, R. Dimitrov, A. Mitchell, M. Stutzmann
- A. S. Cordan, Y. Leroy, A. Goltzené, A. Pépin, C. Vieu, M. Mejias, H. Launois
- Seoung-Hwan Park, Shun-Lien Chuang
- M. O. Aboelfotoh, M. A. Borek, J. Narayan
- A. Saxler, P. Debray, R. Perrin, S. Elhamri, W. C. Mitchel, C. R. Elsass, I. P. Smorchkova, B. Heying, E. Haus, P. Fini, J. P. Ibbetson, S. Keller, P. M. Petroff, S. P. DenBaars, U. K. Mishra, J. S. Speck
- Quoc Toan Le, Li Yan, Yongli Gao, M. G. Mason, D. J. Giesen, C. W. Tang

(Continued)

**MICRON Ex.1070.00006****Micron v. Harvard, IPR2017-00664**

380 Cr/Al and Cr/Al/Ni/Au ohmic contacts to *n*-type GaN

387 Spin-polarized electronic current in resonant tunneling heterostructures

MAGNETISM AND SUPERCONDUCTIVITY (PACS 74-76)

392 Inverse magnetic force microscopy of superconductors in half-space geometry

399 Effect of Zr on the microstructure and magnetic properties of $\text{Sm}(\text{Co}_{0.9}\text{Fe}_{0.1}\text{Cu}_{0.088}\text{Zr}_x)_{8.5}$ magnets

404 Thickness dependent binary behavior of elongated single-domain cobalt nanostructures

410 Exchange coupling of NiFe/CrMnPt_x bilayers prepared by a substrate bias sputtering method

416 Local atomic volume dependence of Tb and Co magnetic moments

419 Magnetic properties and microstructure of $\text{FePt-Si}_3\text{N}_4$ nanocomposite thin films427 Structure, exchange interactions and magnetic anisotropy of $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$ compounds

432 Monte Carlo investigation of transition and compensation temperatures of Fe/Tb multilayers

439 Partitioning behavior of Al in a nanocrystalline FeZrBAl soft magnetic alloy

DIELECTRICS AND FERROELECTRICITY (PACS 77)

443 Dynamical studies of the ferroelectric domain structure in triglycine sulfate by voltage-modulated scanning force microscopy

452 Polarization and structural properties of high-energy electron irradiated poly(vinylidene fluoride-trifluoroethylene) copolymer films

462 Si induced size effects in ferroelectric PbTiO_3

467 Finite-difference modeling of piezoelectric composite transducers

474 Quantum-confinement effects on the optical and dielectric properties for mesocrystals of BaTiO_3 and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ 479 Frequency response of microwave dielectric $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ thin films laser deposited on indium-tin oxide coated glass

484 Hafnium and zirconium silicates for advanced gate dielectrics

DEVICE PHYSICS (PACS 85)

493 Tunable microwave characteristics of a superconducting planar transmission line by using a nonlinear dielectric thin film

498 Effects of nitridation by nitric oxide on the leakage current of thin SiO_2 gate oxides

502 Nonthermal mixing mechanism in a diffusion-cooled hot-electron detector

511 Thermoexcited and photoexcited carrier transports in a GaAs/AlGaAs quantum well infrared photodetector

N. A. Papanicolaou, A. Edwards, M. V. Rao, J. Mittereder, W. T. Anderson

A. Voskoboynikov, Shiue Shin Lin, C. P. Lee, O. Tretyak

Mark W. Coffey

W. Tang, Y. Zhang, G. C. Hadjipanayis

S. Evoy, D. W. Carr, L. Sekaric, Y. Suzuki, J. M. Parpia, H. G. Craighead

Haiwen Xi, Robert M. White

El'ad N. Caspi, Haim Pinto, Mordechai Melamud

Chih-Ming Kuo, P. C. Kuo

Jing-Yun Wang, Bao-Gen Shen, Shao-Ying Zhang, Wen-Shan Zhan, Li-Gang Zhang

L. Veiller, D. Ledue, J. Teillet

M. W. Chen, A. Sakai, A. Inoue, X. M. Wang, Y. Watanabe, T. Sakurai

V. Likodimos, X. K. Orlik, L. Pardi, M. Labardi, M. Allegrini

Vivek Bharti, H. S. Xu, G. Shanthi, Q. M. Zhang, Kuming Liang

V. R. Palkar, S. C. Purandare, P. Ayyub, R. Pinto

John S. Hornsby, D. K. Das-Gupta

Shigemi Kohiki, Syozo Takada, Akihiko Shimizu, Kenichi Yamada, Hirotaka Higashijima, Masanori Mitome

Hsiu-Fung Cheng, Yi-Chun Chen, I.-Nan Lin

G. D. Wilk, R. M. Wallace, J. M. Anthony

Chien-Jang Wu

C. Gerardi, M. Melanotte, S. Lombardo, M. Alessandri, B. Crivelli, R. Zonca

Alex D. Semenov, Gregory N. Gol'tsman

Y. Fu, Ning Li, M. Karlsteen, M. Willander, Na Li, W. L. Xu, W. Lu, S. C. Shen

(Continued)

- 517 On the origin of low frequency noise in GaAs metal-semiconductor field-effect transistors
- 522 Nonuniform quantum well infrared photodetectors

Lech Dobrzański, Zdzisław Wolosiak

S. Y. Wang, C. P. Lee

APPLIED BIOPHYSICS (PACS 87)

- 526 Magnetic and acoustic tapping mode microscopy of liquid phase phospholipid bilayers and DNA molecules

Irène Revenko, Roger Proksch

INTERDISCIPLINARY AND GENERAL PHYSICS (PACS 1-41, 43-47, 79, 81-84, 89-99)

- 534 Near-field probing control of optical propagation in bidimensional guiding mesostructures
- 538 Capacitive ultrasound transducer, based on the electrical double layer in electrolytes
- 543 K₂Te photocathode growth: A photoemission study
- 549 Characterization of ejected particles during laser cleaning
- 553 Atomistic simulation of the vapor deposition of Ni/Cu/Ni multilayers: Incident adatom angle effects
- 564 Effect of mixing enthalpy on relaxed and strained growth of III-V^IV^{II}_{1-y} compound alloys using molecular-beam epitaxy
- 572 Surface oxidation activates indium tin oxide for hole injection
- 577 Buffer free direct growth of GaN on 6H-SiC by metalorganic vapor phase epitaxy
- 584 Electronic properties of CuGaSe₂-based heterojunction solar cells. Part I. Transport analysis
- 594 Electronic properties of CuGaSe₂-based heterojunction solar cells. Part II. Defect spectroscopy

David Mulin, Michel Spajer, Daniel Courjon, Franck Carcenac, Yong Chen

N. Tankovsky

Diego Bisero, Alessandro di Bona, Paola Paradisi, Sergio Valeri

Y. F. Lu, Y. W. Zheng, W. D. Song

X. W. Zhou, H. N. G. Wadley

J. Genoe, Š. Németh, B. Grietens, M. Behet, R. Vounckx, G. Borghs

D. J. Milliron, I. G. Hill, C. Shen, A. Kahn, J. Schwartz

H. Lahreche, M. Leroux, M. Laügt, M. Vaille, B. Beaumont, P. Gibart

V. Nadenau, U. Rau, A. Jasenek, H. W. Schock

A. Jasenek, U. Rau, V. Nadenau, H. W. Schock

COMMUNICATIONS

- 603 Photonic crystal-based resonant antenna with a very high directivity
- 606 Transport properties of NdNiO₃ thin films made by pulsed-laser deposition
- 609 Structural and electrical properties of polycrystalline silicon produced by low-temperature Ni silicide mediated crystallization of the amorphous phase
- 612 Femtosecond studies of coherent acoustic phonons in gold nanoparticles embedded in TiO₂ thin films
- 615 Modal gain and lasing states in InAs/GaAs self-organized quantum dot lasers
- 618 Material gain of bulk 1.55 μm InGaAsP/InP semiconductor optical amplifiers approximated by a polynomial model
- 621 Structural properties of fluorinated amorphous carbon films
- 624 CUMULATIVE AUTHOR INDEX

B. Temelkuran, Mehmet Bayindir, E. Ozbay, R. Biswas, M. M. Sigalas, G. Tuttle, K. M. Ho

G. Catalan, R. M. Bowman, J. M. Gregg

Soo Young Yoon, Seong Jin Park, Kyung Ho Kim, Jin Jang, Chae Ok Kim

W. Qian, L. Lin, Y. J. Deng, Z. J. Xia, Y. H. Zou, G. K. L. Wong

P. W. Fry, L. Harris, S. R. Parnell, J. J. Finley, A. D. Ashmore, D. J. Mowbray, M. S. Skolnick, M. Hopkinson, G. Hill, J. C. Clark

J. Leuthold, M. Mayer, J. Eckner, G. Guekos, H. Melchior, Ch. Zellweger

X. Wang, H. R. Harris, K. Bouldin, H. Temkin, S. Gangopadhyay, M. D. Strathman, M. West

Hafnium and zirconium silicates for advanced gate dielectrics

G. D. Wilk,^{a)} R. M. Wallace,^{b)} and J. M. Anthony^{c)}

Central Research Laboratories, Texas Instruments, Dallas, Texas 75243

(Received 12 May 1999; accepted for publication 21 September 1999)

Hafnium and zirconium silicate (HfSi_xO_y and ZrSi_xO_y , respectively) gate dielectric films with metal contents ranging from ~ 3 to 30 at. % Hf, or 2 to 27 at. % Zr (± 1 at. % for Hf and Zr, respectively, within a given film), have been investigated, and films with ~ 2 –8 at. % Hf or Zr exhibit excellent electrical properties and high thermal stability in *direct contact* with Si. Capacitance–voltage measurements show an equivalent oxide thickness t_{ox} of about 18 Å (21 Å) for a 50 Å HfSi_xO_y (50 Å ZrSi_xO_y) film deposited directly on a Si substrate. Current–voltage measurements show for the same films a leakage current of less than 2×10^{-6} A/cm² at 1.0 V bias. Hysteresis in these films is measured to be less than 10 mV, the breakdown field is measured to be $E_{\text{BD}} \sim 10$ MV/cm, and the midgap interface state density is estimated to be $D_{\text{it}} \sim 1$ – 5×10^{11} cm⁻² eV⁻¹. Au electrodes produce excellent electrical properties, while Al electrodes produce very good electrical results, but also react with the silicates, creating a lower ϵ layer at the metal interface. Transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy indicate that the dielectric films are amorphous silicates, rather than crystalline or phase-separated silicide and oxide structures. TEM shows that these films remain amorphous and stable up to at least 1050 °C in direct contact with Si substrates. © 2000 American Institute of Physics. [S0021-8979(00)00701-5]

I. INTRODUCTION

The prospect of replacing silicon dioxide as the gate dielectric material for standard complementary metal oxide semiconductor (CMOS) technology is a formidable task, considering that SiO_2 has been used successfully for decades and its properties are understood as well as those of any dielectric. The area of advanced gate dielectrics has gained considerable attention recently because technology roadmaps predict the need for a sub-20 Å Si–oxide gate dielectric for sub-0.13 μm CMOS. It has been demonstrated that, for both a 15 and a 13 Å gate oxide,^{1,2} a transistor intended for high-performance applications can operate with high leakage currents of 1–10 A/cm² at V_{DD} . Transistors intended for low-power use, such as application specific integrated circuits and wireless products, however, require lower leakage currents. There are also significant reliability concerns for SiO_2 in this thickness regime, regardless of the transistor application.³ Some approaches have focused on surface preparation as a way to provide a flatter, more uniform Si interface, and thereby minimize electron channel mobility degradation and gate leakage.^{4–6} Growing or depositing sub-15 Å oxides has also been investigated as a potential means for producing high-quality, reproducible, and uniform gate oxides, either for use as the gate dielectric or as the bottom layer of a dielectric stack.^{7,8}

Recent efforts on alternate gate dielectrics have been focused on materials structures such as oxynitrides and oxide/nitride stacks, which provide a slightly higher ϵ value (and

are therefore physically thicker) for reduced leakage, improved resistance to boron diffusion, and better reliability characteristics.^{9–11} It appears that these approaches with oxide or oxide–nitride combinations will work well down to an equivalent oxide thickness t_{ox} of $t_{\text{ox}} \sim 15$ Å, but below this, either gate leakage or electron channel mobility degradation effects will most likely prevent further improvements in device performance. As an alternative to oxide/nitride systems, much work has been done on high- ϵ metal oxides as a means to provide a substantially thicker (physical thickness) dielectric for reduced leakage and improved gate capacitance. Work is ongoing for materials systems such as Ta_2O_5 ,^{12–15} TiO_2 ,¹⁶ SrTiO_3 ,¹⁷ Al_2O_3 ,¹⁸ and Zr-Sn-Ti-O ,¹⁹ which have ϵ values ranging from 10 to 80, but these have been employed mainly due to their maturity in memory capacitor and microwave applications, and the resultant semiconductor manufacturing tool development infrastructure. Most of these films, however, are not thermally stable in direct contact with Si. In particular, interfacial reaction has been observed for the cases of Ta_2O_5 and TiO_2 on Si.^{20,21} For this reason, these metal oxides require that both the gate and the channel interfaces be modified to limit the amount of reaction.

Interface engineering schemes have been developed to form oxynitrides and oxide/nitride reaction barriers between the high ϵ metal oxide material and Si in an attempt to prevent or at least minimize reaction with the underlying Si.^{12–16} While these barrier layers have been shown to reduce the extent of reaction between the high- ϵ dielectric and Si, the increased process complexity for the deposition and control of additional ultrathin dielectric layers, as well as scalability to later technology nodes, is a large concern. Even in the ideal case of completely eliminating interfacial reaction, however, the structure still contains several dielectrics in se-

^{a)}Present address: Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974-0636; electronic mail: gwilk@lucent.com

^{b)}Present address: Mat. Sci. Dept., Univ. of North Texas, P.O. Box 305310, Denton, TX 76203-5310.

^{c)}Present address: Center for Microelectronics Research, Univ. of South Florida, Tampa, FL 33620-5350.

ries, where the lowest capacitance layer will dominate the overall capacitance and also set a limit on the minimum achievable t_{ox} value.²²

It is therefore highly desirable to use an advanced gate dielectric which is stable on Si, and which exhibits a Si interface quality comparable to that of SiO_2 . This would avoid the need for an interfacial layer and at the same time, the high ϵ value of the material could be fully utilized. Previous work on alternate dielectrics, as discussed below, investigated materials systems such as ZrO_2 and HfO_2 for the purpose of optical coatings and DRAM applications. Consideration of this work is also useful for gate dielectric applications.

Examination of sputtered ZrO_2 - SiO_2 codeposited, thick (~ 3000 Å) films has been reported by Russack and co-workers.²³ X-ray diffraction analysis of the films indicated that the films with $>10\%$ SiO_2 remain amorphous even upon annealing at 500°C in air for 60 hs. Films with $<10\%$ SiO_2 exhibited a crystalline ZrSiO_4 diffraction pattern under similar annealing conditions. Composition analysis of their films, as deduced by RBS, indicated that the films have a metal:oxygen ratio of 1:2, signifying that they are fully oxidized.

Roberts *et al.* investigated HfO_2 : SiO_2 films also prepared by sputter techniques.²⁴ They found that Hf-silicate films provided superior performance to sputtered Ta_2O_5 films for thin capacitor insulator film thicknesses (100–150 Å range). A preferred stoichiometry of $\text{Hf}_4\text{SiO}_{10}$ was identified as a result of breakdown measurements and $\epsilon=13$ was reported. It was noted that interfacial SiO_2 growth occurs upon subsequent O_2 annealing above 800°C for $\text{Hf}_x\text{SiO}_{2x+2}$, where $x<2$ or $x>4$. Additionally, investigation of interface engineering using SiO_2 /Hf $_4$ SiO $_{10}$ /Si $_3$ N $_4$ insulator stacks provided improved performance compared to similar structures incorporating Ta_2O_5 .

Balog *et al.*²⁵ have performed capacitance-voltage (C - V) measurements on very thick (~ 3000 – 4000 Å) polycrystalline HfO_2 films in Al/HfO $_2$ /Si structures. For films grown (by CVD) at 450°C in pure O_2 , a large hysteresis was observed. It was indicated that subsequent anneals in inert ambients, such as in N_2 at 800°C , will lead to a reduction in the observed hysteresis. However, HfO_2 films grown at $T \geq 500^\circ\text{C}$ result in no observed hysteresis and $D_{\text{it}} \sim 1$ – $6 \times 10^{11}/\text{cm}^2$. Breakdown fields for these films were reported to be ~ 1 – 2 MV/cm and $\epsilon=22$ – 25 at 1 MHz was reported. Balog *et al.* also found essentially identical results for ZrO_2 films in Al/ ZrO_2 /Si structures.²⁵ The dielectric constant for these films ranged from 17 to 18. However, we note that the reported Si surface preparation procedure most likely resulted in the formation of a native oxide prior to HfO_2 and ZrO_2 deposition.

Shappir *et al.* examined thinner (300–600 Å) ZrO_2 films (deposited by metalorganic CVD at 450°C) in various MIS structures (with a native oxide on the substrate) that included Al, Mo, and poly-Si gates.²⁶ For Al gate capacitors, annealing at $T \geq 800^\circ\text{C}$ in N_2 resulted in a large reduction in leakage current. Interestingly, anneals in O_2 /HCl at 800°C resulted in the largest reduction in leakage, although no reduction in the measured dielectric constant (due to poten-

tial SiO_2 formation) was observed. Breakdown fields of 4 MV/cm were reported for the subsequently annealed films. A large hysteresis was observed in all C - V curves, with a shift of ~ 600 mV for unannealed and N_2 -annealed samples, and a shift of ~ 200 mV for O_2 /HCl-annealed samples. These films were estimated to have $D_{\text{it}} \sim 1 \times 10^{12}/\text{cm}^2$, which may have been even higher from the polycrystalline ZrO_2 were it not for the presence of the native oxide. A dielectric constant at 1 MHz ranging from 14 to 19 was observed (ϵ decreased with increasing anneal temperature), even with the native oxide present. Leakage currents in these very thick films was reported to be as low as 8×10^{-9} A/cm 2 at 1.5 MV/cm.

Mo gate devices exhibited similar dielectric constants with a higher ($\sim 10\times$) loss tangent than that for the Al gate structures. Leakage currents were somewhat higher and breakdown was observed at a slightly lower value (~ 3.7 MV/cm). Since Mo has a larger work function ($\Phi_B = 4.5$ eV) than that of Al ($\Phi_B = 4.3$ eV), Mo is expected to result in a lower tunneling current for gate injection, but apparently reaction at the gate interface altered the tunneling properties. The increase in the leakage current was attributed to MoO or MoN formation during the postdeposition annealing process.

It was found that poly-Si gates produced good performance when the amorphous Si was deposited at 550°C , followed by a POCl_3 doping (885°C) and drive step (920°C for 2.5 h), which also served to crystallize the Si electrode. (It was reported that poly-Si deposition at higher temperatures (620°C) results in the reduction of ZrO_2 to form a Zr-rich layer near the poly-Si/ ZrO_2 interface, leading to very high leakage currents.) Leakage currents were comparable to those observed for the Al or Mo gate structures, but the reported breakdown field was lower than Al, ~ 3 MV/cm. A dielectric constant of $\epsilon \sim 16$ was measured, again with the presence of a native oxide.

The large hysteresis and other shifts in the C - V curves were observed for all of the electrodes and annealing conditions used in this study, which indicates that the shifts probably arise from mobile ion transport in the pure ZrO_2 films.²⁷ All of these studies on ZrO_2 and HfO_2 indicate crystallization of the metal oxides either during the deposition process or upon moderate postannealing conditions.

An important approach toward predicting and understanding the relative stability of a particular three-component system for device applications can be explained through ternary phase diagrams.^{28,29} An analysis of the Gibbs free energies governing the relevant chemical reactions for the Zr-Si-O system leads to the ternary phase diagram shown in Fig. 1. The tie lines in the phase diagram for the Zr-Si-O system,³⁰ indicate that the metal oxide ZrO_2 and the compound silicate ZrSiO_4 will both be stable in direct contact with Si up to high temperature. The gray shaded area in Fig. 1 denotes a large field of ZrSi_xO_y compositions which are expected to be stable on Si up to high temperatures. Other ZrSi_xO_y compositions outside of the gray area are also stable on Si, but since it is desirable to prevent any Zr-Si bonding, film compositions within the gray area are preferable. Furthermore, even within the shaded area, compositions with high O levels (closer to ZrSiO_4) are preferred because this

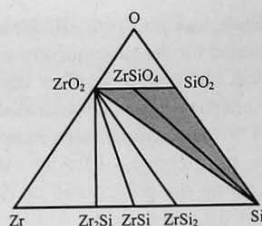


FIG. 1. Ternary phase diagram for the Zr-Si-O system. The tie lines indicate that both ZrO_2 and ZrSiO_4 , as well as ZrSi_xO_y silicates, are stable in direct contact with Si. The gray shaded area indicates a region of ZrSi_xO_y compositions which are expected to be desirable for gate dielectrics. This figure is redrawn from Wang and Mayer (see Ref. 30).

will be more likely to prevent M-Si bonding ($\text{M}=\text{Zr}$ or Hf) for silicide phase formation. In fact, the existence of this large phase field of stable ZrSi_xO_y compositions implies yet another potential advantage, in that the level of Zr (or Hf) incorporated into the silicate film could be gradually increased from one technology node to the next. This gradual shift in film composition could provide a continually higher ϵ value (up to a point), as is needed to meet device performance requirements.

This behavior is expected to be the same for the Hf-Si-O system based on coordination chemistry arguments. Although the thermodynamic information is incomplete for the Hf-Si-O system, the available data suggest that HfO_2 and HfSiO_4 , as well as a large range of HfSi_xO_y compositions, will be stable in direct contact with Si up to high temperatures.³¹⁻³³ This thermal stability is extremely important, because it suggests that there is potential to control the dielectric-Si interface. Although some schemes attempt to avoid thermal instabilities of other high- ϵ materials by using process modifications such as a replacement gate flow,¹² which allows the high-temperature processing to be done before deposition of the final gate dielectric, the continued thermal cycling afterward is sufficient to result in poor electrical properties.¹² It is therefore important to select a materials system in which the desired final state is a stable one.

Both HfO_2 and ZrO_2 have high dielectric constants and are thermally stable on Si, and therefore are potential gate dielectrics, but there are several concerns associated with these metal oxides. As mentioned previously, these oxides are ionic conductors,²⁷ as O ions can diffuse through the oxides and leave vacancies behind, which then can act as traps and reliability concerns. Furthermore, both ZrO_2 and HfO_2 tend to crystallize at low temperatures, leading to polycrystalline films, with high-leakage paths along grain boundaries and nonuniformities in ϵ value and in film thickness. Low-temperature deposition and processing may be used in an attempt to prevent crystallization, but it is likely that the thermal cycles required in fabricating a transistor would cause the films to crystallize. The heterointerface formed between the ZrO_2 or HfO_2 and Si may also lead to a large amount of channel electron mobility degradation, which may be manifested only in transistors and not in capacitor structures. A better approach is apparent: use a silicate dielectric from the onset.

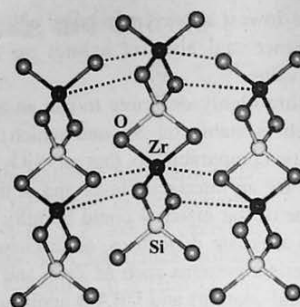


FIG. 2. Atomic model of several chain portions of the crystalline structure for ZrO_2 - SiO_2 (zircon), as described by Blumenthal (see Ref. 36). Black atoms=Zr (or Hf), white atoms=Si, gray atoms=O. Dashed lines represent bonds between Zr (or Hf) atoms of a given chain and O atoms of neighboring chains, which provide a three-dimensional stability to the structure. Similar bonds exist between Zr atoms of a given chain and other O atoms of neighboring chains, but are not shown for clarity.

Zirconium and hafnium silicates (ZrSi_xO_y and HfSi_xO_y , respectively) are also stable in direct contact with Si, and by controllably incorporating a suitably high level of Si during deposition, the dielectric-Si interface will act more like the preferable SiO_2 -Si interface, and the driving force is removed for any reaction between the substrate and the dielectric. The use of ZrSi_xO_y (and therefore HfSi_xO_y) should allow for control of the Si interface, which removes the key problem that has limited other high- ϵ gate dielectric material approaches at the channel interface, and also affords the significant flexibility of continued use of poly Si-based gates. Furthermore, midgap work function metal gate systems have been predicted not to provide a performance improvement worthy of the added process complexity to replace Si-based gates.³⁴ The ϵ values of HfSi_xO_y and ZrSi_xO_y are substantially lower than those of pure HfO_2 and ZrO_2 , but this tradeoff for interfacial control will be acceptable as long as the resulting leakage currents are low enough. As a note on the Hf-Si-O system, hafnium suffers the misconception that it is radioactive, but this is not the case.³⁵

There has been much less information reported on HfSi_xO_y than on ZrSi_xO_y , but the chemical similarities between Hf and Zr allow for comparison between the respective silicate systems. As described by Blumenthal,³⁶ and Bragg *et al.*,³⁷ the Bravais lattice for the stoichiometric compound ZrSiO_4 (zircon) is body-centered tetragonal, and belongs to point group D_{4h} . The crystal is composed of SiO_4 tetrahedra interspersed with Zr atoms, but can be considered as parallel chains of ZrO_2 and SiO_2 structural unit molecules, as shown in Fig. 2. Each Zr and Si atom shares bonds to four O atoms within each chain, and each successive pair of O atoms is oriented in a transverse configuration, forming ZrO_2 and SiO_2 units. The Si-O bond length is shorter than the Zr-O bond length within a chain (not represented in the figure). Figure 2 shows that each Zr atom also shares bonds with other O atoms in neighboring chains (only two of the four bonds to neighboring chains are shown for each Zr atom, for clarity), providing a three-dimensional stability to the material.

It is important to note that each Zr and Si atom has only O atoms as nearest neighbors. Chemical analysis of homogeneous silicate films is therefore expected to show only Zr–O nearest-neighbor bonding, with a slight effect from Si as a next-nearest neighbor. Although the films presented in this study are amorphous, it is reasonable to assume that for Hf and Zr concentrations less than that of the stoichiometric $\text{MO}_2\text{--SiO}_2$ compound, nearly all bonds will be Zr–O (or Hf–O) and Si–O bonds.

Using coordination chemistry arguments between Hf and Zr, HfSiO_4 should have the same structure as ZrSiO_4 . A value of $\epsilon = 12.6$ for ZrSiO_4 is reported by Blumenthal,³⁶ which is reasonable considering that this structure is comprised of SiO_2 ($\epsilon = 3.9$) and ZrO_2 ($\epsilon = 25$) components. Similarly, since HfO_2 has reported values^{25,38} of $\epsilon = 25\text{--}40$, an HfSiO_4 compound is expected to have a range of $\epsilon = 15\text{--}25$. The exact value of ϵ will certainly depend strongly on film composition, density, and structure, since amorphous materials, which are used in this study, typically have less lattice polarizability than their crystalline counterparts. Considering all of the desired properties, HfSi_xO_y and ZrSi_xO_y should be excellent materials candidates for advanced gate dielectrics, and indeed some very encouraging results have been previously reported.^{39,40}

Finally, the potential use of silicates as a replacement for SiO_2 gate dielectrics should not be viewed as a significant departure from the historical progression of dielectrics in CMOS technology. Silicon dioxide has been unimaginably ideal for integrated circuits, because it has been used for decades both as the interlevel dielectric (ILD) between successive metal interconnect levels and as the gate oxide for MOSFETs. Recent technology demands, however, have required that SiO_2 in the ILD be modified to create a lower dielectric constant, so that lower RC time delays can be achieved. These changes have been made by simply incorporating H, F, and C into the SiO_2 to lower the ϵ value of the oxide. These modifications, while certainly not trivial, have thus far proved to be manageable and integrable.

Similar demands for higher drive currents and lower leakage have required SiO_2 in the gate dielectric to be altered by adding N, both in the form of doping and as a silicon nitride layer on top of SiO_2 . This process slightly increases the effective dielectric constant, allowing use of a physically thicker film, and thereby achieves a higher drive current with less leakage. With these trends in mind, silicate gate dielectrics should also be viewed as only another modification of SiO_2 , in this case by “doping” with Zr or Hf, to further improve device performance while remaining compatible with the rest of well-established CMOS processing procedures. In fact, if these silicate films can be used, then by simply increasing the “doping” level of Zr or Hf from one technology node to the next for gradually improved device performance, this same materials system should fulfill the requirements on current roadmaps until the year 2010.

In this study, it is shown that a thin dielectric layer of HfSi_xO_y or ZrSi_xO_y yields a t_{ox} value ranging from 18 to 22 Å with a leakage current density less than 2×10^{-6} A/cm², while remaining in a glassy, amorphous state in direct contact with Si during anneals up to 1050 °C for 20 s. The physical

and electrical properties of HfSi_xO_y and ZrSi_xO_y dielectric films are described based on the results of a variety of analysis techniques.

II. EXPERIMENT

Substrates were 4 in. *n*- and *p*-type Si(100) wafers, both with $\rho = 0.01\text{--}0.02$ Ω cm. Samples were prepared by etching in a buffered (1%) HF solution for approximately 20 s, leaving an H-terminated surface. Once under vacuum, hydrogen was desorbed by annealing the wafer at 700 °C for 10 min. The silicate films were deposited by two methods. Most silicates were sputter deposited in a system with a base pressure of 5×10^{-9} Torr, with sputter rates of 5–6 Å/min and substrate temperatures ranging from 25 to 600 °C. The substrates were heated radiatively from the back side, with an absolute temperature accuracy of ± 20 °C over the temperature range used. Some silicate films were deposited by *e*-beam evaporation in an ultrahigh vacuum (UHV) chamber, with a base pressure of 7×10^{-11} Torr and deposition rates of 2–10 Å/s. Substrate temperature range and heating method were the same as the case for sputtering. Films with high Hf and Zr levels (up to 30 at. %) were achievable by this method, but the electrical properties of these films were typically poor. In this article, therefore, only physical characterization is presented on films deposited by *e*-beam evaporation in the UHV system.

Capacitors were formed using Au and Al *ex situ* thermal evaporation at room temperature, followed by photolithography and wet etching steps to pattern the electrodes. *C*–*V* measurements were performed in parallel mode on an HP 4284 LCR meter at frequencies up to 1 MHz. Capacitor areas ranged from 10^{-6} to 10^{-2} cm², and both capacitance and current scaled linearly with area, indicating uniform, high-quality films.

III. RESULTS AND DISCUSSION

A. Physical characterization

Figure 3 shows high-resolution TEM images of a 50 Å $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film before and after annealing. Figure 3(a) shows the as-deposited film, which was sputter deposited at a substrate temperature of 500 °C, with an Au cap. The HfSi_xO_y –Si interface is seen to be atomically sharp, and the silicate is completely amorphous. Figure 3(b) shows the same film after an anneal at 800 °C for 30 min in a N_2 ambient (Au deposited after anneal). The film remains amorphous, the interface remains sharp, and the thickness of the layer shows no visible change after anneal at high temperature, which demonstrates the stability of HfSi_xO_y films in direct contact with Si. Au lattice fringes are visible in both (a) and (b).

Figure 4 shows high-resolution TEM images of a 50 Å $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ film before and after annealing. Figure 4(a) shows the as-deposited film, which was sputtered at room temperature, with an Al cap. The ZrSi_xO_y –Si interface is seen to be atomically sharp, within the region of the TEM image, and the silicate is completely amorphous. It should be noted that all of the samples studied showed similarly sharp interfaces

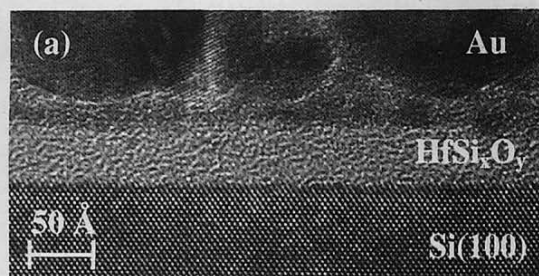


FIG. 3. TEM cross section of a 50 Å $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film with an Au cap (a) as-deposited at 500 °C and (b) after annealing at 800 °C for 30 min in N_2 . The silicate film remains amorphous and stable, with no sign of reaction after the anneal.

FIG. 5. TEM cross section of a ~ 30 Å $\text{Hf}_7\text{Si}_{29}\text{O}_{64}$ film with a Si cap (a) as-deposited at 500 °C and (b) after annealing at 1050 °C, for 20 s in N_2 . The amorphous Si cap crystallized during the anneal, but the film remained amorphous and stable, while maintaining atomically sharp interfaces with both the substrate and the cap layer.

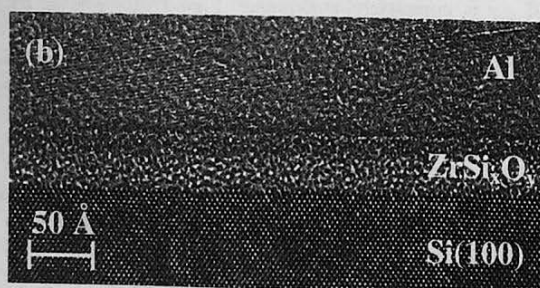
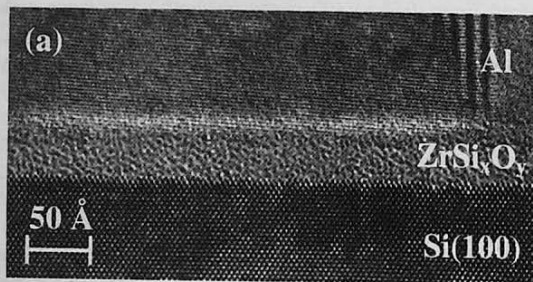


FIG. 4. TEM cross section of a 50 Å $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ film with an Al cap (a) as-deposited at 500 °C and (b) after annealing at 800 °C for 30 min in N_2 . The silicate film remains amorphous and stable, but the slight contrast difference at the Al interface indicates possible reaction.

for samples taken from all across the wafers. The termination of the Al lattice fringes on the silicate layer clearly denotes the top interface. Figure 4(b) shows the same film after an anneal at 800 °C for 30 min in a N_2 ambient (Al deposited after anneal). As in the case of $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$, the interface remains sharp and the thickness of the layer shows no visible change after anneal at high temperature. There is a slight contrast difference visible in the $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ layer near the top Al interface in both images. It is possible that this contrast difference arises from some slight reaction of the Al electrode with the ZrSi_xO_y film. Similar contrast is visible for the case of Al on HfSi_xO_y films, but no such contrast differences are visible for Au electrodes on either HfSi_xO_y or ZrSi_xO_y films. Evidence of Al-silicate reaction will be further discussed below in Sec. III B.

Figure 5 shows TEM images of a ~ 30 Å $\text{Hf}_7\text{Si}_{29}\text{O}_{64}$ film, sputter deposited at 500 °C, with a Si cap, before and after annealing. In Fig. 5(a), an amorphous Si layer has been deposited at 25 °C to provide a capping layer on the silicate. Both interfaces are seen to be atomically sharp, with no signs of reaction, and the silicate film is completely amorphous. Figure 5(b) shows the same film after rapid thermal annealing at 1050 °C for 20 s, which emulates a dopant activation anneal. It can be seen that while the top Si layer has crystallized into poly-Si, the silicate film remains entirely unchanged. The $\text{Hf}_7\text{Si}_{29}\text{O}_{64}$ film is still completely amorphous and is the same thickness as before the anneal, while both Si interfaces have remained atomically sharp. These observations confirm the predictions made by thermodynamics, and indicates that by using silicates, the interface can indeed be

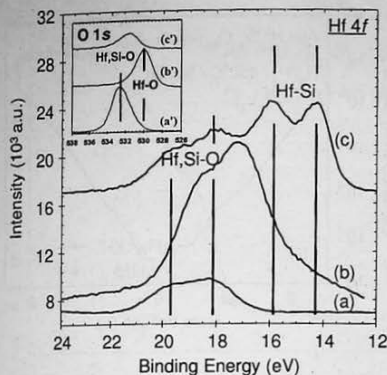


FIG. 6. Hf 4f XPS features for: (a) thin $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film, (b) thick HfO_2 film, and (c) thick O-rich HfSi_2 film. No evidence of Hf-Si bond formation is observed for the Hf-silicate film. (Inset) Oxygen 1s XPS features for: (a') thin $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film, (b') thick HfO_2 film, and (c') thick O-rich HfSi_2 film. Silicate formation (vs metal-oxide) is confirmed by the O 1s feature.

controlled up to the required thermal processing treatments, while the film remains in a glassy phase.

Chemical characterization of various HfSi_xO_y and ZrSi_xO_y films was accomplished by x-ray photoelectron spectroscopy (XPS) utilizing monochromatic and standard Al x-ray sources. Figure 6 shows a comparison of the Hf 4f features for: (a) a thin, 53 Å $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film to very thick, (b) HfO_2 , and (c) HfSi_2 films. The intensity of (a) is much less than that of (b) and (c) because the HfO_2 and HfSi_2 films were much thicker than the silicate film. (The HfSi_2 film has residual oxygen contamination from the deposition ambient and is thus perhaps more properly described as an "O-rich" HfSi_2 film.). It can be seen that curve (a) exhibits features consistent with the formation of Hf-O bonding in the vicinity of Si. No evidence (within detectable limits) of Hf-Si bond formation in the $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film is observed, as the Hf 4f doublet for Hf-Si bonding, shown in (c), is widely separated from that due to Hf-O bonding (in the vicinity of Si). This lack of Hf-Si bonding is expected in the HfSi_xO_y

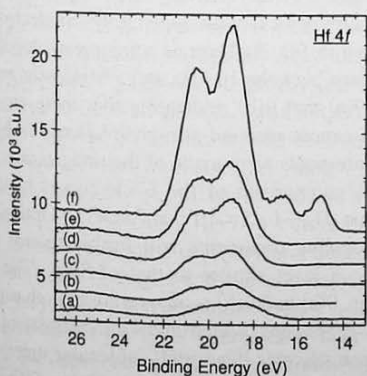


FIG. 7. XPS spectra of the Hf 4f region for sputtered and e-beam evaporated HfSi_xO_y films. Sputtered $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ films at: (a) 25 °C; (b) 300 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C; $\text{Hf}_{28}\text{Si}_{30}\text{O}_{42}$ film evaporated at (f) 600 °C. The evaporated film clearly shows peaks for Hf-Si silicide bonding, whereas none of the sputtered films show Hf-Si peaks.

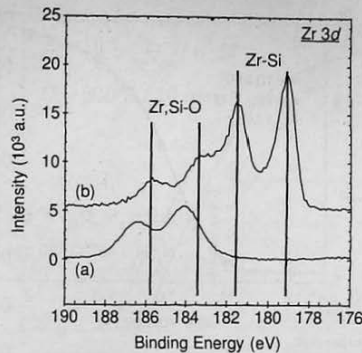


FIG. 8. XPS data with Zr 3d features of: (a) a $\text{Zr}_5\text{Si}_{31}\text{O}_{64}$ film and (b) an O-rich ZrSi_2 film. No evidence of Zr-Si bond formation is observed for the Zr-silicate film.

films, based on the structural model of ZrSiO_4 described earlier, which shows that Zr (or Hf) and Si atoms, respectively, are only bonded to O atoms as nearest neighbors. The data in Fig. 6 are consistent with the formation of a silicate film without phase separation into silicides. Indeed, comparison of the Hf 4f features for curves: (a) $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ and (b) HfO_2 films in Fig. 6 confirms that the bonding in (a) is consistent with a silicate rather than a metal oxide. This is also evident by inspection of the O 1s features for these samples, shown in the Fig. 6 inset. The observed O 1s binding energy of ~532 eV is consistent with a silicate bond rather than a metal-oxide bond (~530 eV).

Figure 7 shows the monochromatic XPS spectra for various HfSi_xO_y films as a function of thickness. These data were charge corrected by aligning the Si substrate spectral feature to 99.5 eV.⁴¹ The Hf 4f feature intensity increases with thickness, as expected. Figure 7 shows a comparison of XPS spectra for several HfSi_xO_y films, deposited by both sputtering at temperatures ranging from 25 to 600 °C [curves (a)–(e)] and e-beam evaporation at 600 °C [curve (f)]. The evaporated film shows clear peaks associated with Hf-Si bonding, which are not present in the sputtered films. All evaporated silicates showed evidence of silicide bonding, regardless of deposition temperature, whereas none of the sputtered films showed silicide bonding. The silicide bonding may be a result of the specific e-beam evaporation conditions used. As mentioned previously, any silicide formation is highly undesirable, and this is in part responsible for the poor electrical properties measured for the evaporated films. Preliminary time-of-flight secondary mass ion spectroscopy analysis (not shown here) also indicates the presence of Hf-Si and Zr-Si fragments for the evaporated films, which is a further indication of silicide bonding.

Similar data were obtained for the ZrSi_xO_y films. Figure 8 presents a comparison of the Zr 3d region for: (a) a 160 Å $\text{Zr}_5\text{Si}_{31}\text{O}_{64}$ film to that obtained for (b) an O-rich ZrSi_2 film after Ar sputtering. It can again be seen that the film obtained is a silicate with no evidence of Zr-Si bond formation within detectable limits. The expected increase in the Zr intensity as a function of thickness was also observed (not shown).

Rutherford backscattering spectrometry and XPS measurements agreed well, and showed typical Hf film compo-

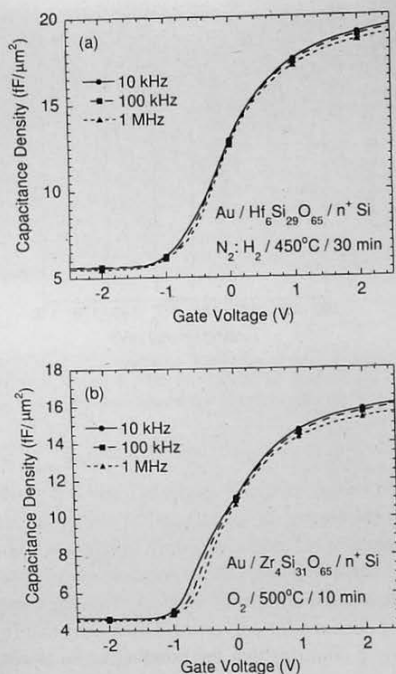


FIG. 9. C - V curves of thin $\text{HfSi}_3\text{O}_{65}$ and $\text{ZrSi}_3\text{O}_{65}$ films, with Au electrodes ($A = 1.76 \times 10^{-4} \text{ cm}^2$): (a) 50 Å $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film on n^+ Si, deposited at 500°C , and subsequently annealed in forming gas at 450°C for 30 min. The C_{max}/A value in accumulation yields $t_{\text{ox}} = 17.8 \text{ Å}$; (b) 50 Å $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ film on n^+ Si, deposited at 25°C , and subsequently annealed in O_2 at 600°C for 10 min. The capacitance density in accumulation yields $t_{\text{ox}} = 20.8 \text{ Å}$. These films have some dispersion near zero bias which indicates the presence of interface traps.

sitions to be approximately $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ (± 1 at. % for Hf). Depending on deposition conditions, however, the composition ranged down to $\text{Hf}_3\text{Si}_{30}\text{O}_{67}$ or up to $\text{Hf}_{30}\text{Si}_{10}\text{O}_{60}$ (obtained by e -beam deposition). Typical Zr films had compositions of $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ (± 1 at. % for Zr), but overall ranged from $\text{Zr}_7\text{Si}_{32}\text{O}_{66}$ to $\text{Zr}_{27}\text{Si}_{15}\text{O}_{58}$ (highest Zr levels obtained by e -beam evaporation). Further data accumulation by XPS may allow determination of other physical properties of these silicates, such as the inelastic mean free path for electrons.⁴²

B. Electrical characterization

The C - V characteristics of thin HfSi_xO_y and ZrSi_xO_y films are shown in Fig. 9. A plot of the C - V curves for an $\text{Au}/50 \text{ Å} \text{Hf}_6\text{Si}_{29}\text{O}_{65}/n^+$ Si structure are shown in Fig. 9(a), with an electrode area of $1.76 \times 10^{-4} \text{ cm}^2$. The silicate film was deposited directly on Si at 500°C and postannealed in forming gas (90% N_2 :10% H_2) at 450°C for 30 min. The largest value of measured capacitance density in accumulation is $C_{\text{max}}/A = 19.3 \text{ fF}/\mu\text{m}^2$, which corresponds to $\epsilon \sim 11$, or an equivalent oxide thickness of $t_{\text{ox}} = 17.8 \text{ Å}$, where t_{ox} is the electrical thickness equivalent for pure SiO_2 .⁴³ This is the first reported oxide equivalent below 20 Å for a single layer advanced gate dielectric deposited directly on Si. Figure 9(b) shows the C - V curves for an $\text{Au}/50 \text{ Å} \text{Zr}_4\text{Si}_{31}\text{O}_{65}/n^+$ Si structure, which also has an electrode area of 1.76

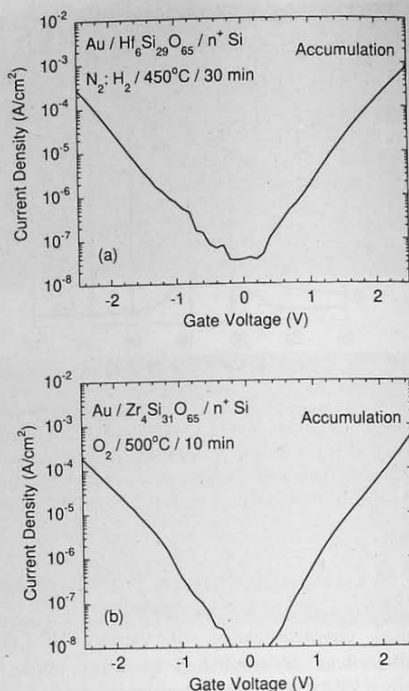


FIG. 10. I - V curves for films shown in Fig. 9: (a) $\text{Au}/50 \text{ Å} \text{Hf}_6\text{Si}_{29}\text{O}_{65}/n^+$ Si. (b) $\text{Au}/50 \text{ Å} \text{Zr}_4\text{Si}_{31}\text{O}_{65}/n^+$ Si. These films show extremely low leakage currents, which are below $2 \times 10^{-6} \text{ A/cm}^2$ at 1.0 V in accumulation. The I - V curves are well behaved, and appear nearly symmetrical about zero bias. This suggests nearly equal barrier heights in both polarities.

$\times 10^{-4} \text{ cm}^2$. The silicate film was deposited directly on Si at 25°C and postannealed in O_2 at 600°C for 10 min. The largest value of measured capacitance density in accumulation corresponds to an equivalent oxide thickness of $t_{\text{ox}} = 20.8 \text{ Å}$. This is a very promising t_{ox} value, considering that the film was deposited directly on Si.

Figure 9 also demonstrates that the Au electrode, with a work function $\Phi_B = 5.3 \text{ eV}$,⁴⁴ creates a flatband condition at zero bias ($V_{\text{fb}} \sim 0 \text{ V}$). Au was chosen for its chemical inertness and because of its relatively large Φ_B . Work is underway to measure devices with doped poly-Si electrodes, such as that shown in Fig. 5. There is a frequency dependence of the capacitance between 10 kHz and 1 MHz near zero bias in both Figs. 9(a) and 9(b), indicating that there are interface traps which cannot respond at high frequency. Although no direct measurements were made of the midgap interface state density D_{it} , comparison of the C - V curves to ideal ones indicates that $D_{\text{it}} \sim 1\text{--}5 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$. Optimization of the postprocessing treatments will further reduce the interface traps to a level similar to that of SiO_2 . The 100 kHz curve in Figs. 9(a) and 9(b) is an overlay of both positive and negative C - V sweeps, which gives a hysteresis of less than 10 mV . Since silicates have SiO_2 molecular units, and have similar Si-O bond lengths (1.62 Å) to pure SiO_2 , it is not surprising that forming gas sinters work well for these materials.

The corresponding current-voltage (I - V) characteristics for the films represented in Fig. 9 are shown in Fig. 10.

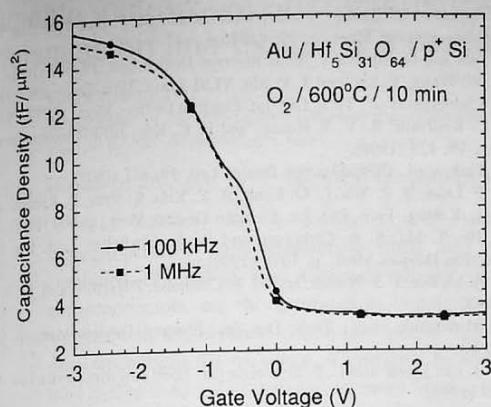


FIG. 11. C - V curves of a 65 Å $\text{Hf}_5\text{Si}_{31}\text{O}_{64}$ film on p^+ Si, deposited at 500 °C, followed by anneal in forming gas (90% N_2 :10% H_2) at 450 °C for 30 min, with Au electrodes ($A = 1.76 \times 10^{-4} \text{ cm}^2$). The capacitance density at C_{max} corresponds to $t_{\text{ox}} = 21.2$ Å. The dispersion near zero bias indicates interface traps, and $V_{\text{fb}} \sim -1$ V, which is expected since $V_{\text{fb}} \sim 0$ V for a similar on n^+ Si, as shown in Fig. 9.

Figure 10(a) displays the I - V characteristics for the Au/50 Å $\text{Hf}_6\text{Si}_{29}\text{O}_{65}/n^+$ Si sample shown in Fig. 9(a), with the same Au electrode area. The leakage current density is very low for this film, ranging from 10^{-6} to 10^{-5} A/cm^2 in the bias range from 1.0 to 1.5 V. A pure SiO_2 layer of the same electrical ~ 18 Å thickness⁴⁵ has a current density of approximately 1 A/cm^2 , nearly six orders of magnitude higher leakage current than that for an electrically equivalent $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film. Although these results use an Au electrode ($\Phi_B = 5.3 \text{ eV}$) and the leakage characteristics of SiO_2 reported in Ref. 45 used an Al electrode ($\Phi_B = 4.3 \text{ eV}$), leakage currents measured on both the HfSi_xO_y and ZrSi_xO_y films showed only a $\sim 2\times$ increase for Al electrodes compared to Au. The order of magnitude comparison of the SiO_2 and HfSi_xO_y or ZrSi_xO_y leakage currents is therefore valid. Figure 10(b) shows the I - V plots for the Au/50 Å $\text{Zr}_4\text{Si}_{31}\text{O}_{65}/n^+$ Si sample in Fig. 9(b). The leakage current density is very low, as $J = 7 \times 10^{-7} \text{ A/cm}^2$ at a bias of 1.0 V. Similar to the $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film in Fig. 10(a), the $\text{Zr}_4\text{Si}_{31}\text{O}_{65}$ film in Fig. 10(b) shows an enormous reduction in leakage current over a comparable, electrically equivalent thickness of a pure SiO_2 layer.⁴⁵ The overall greatly reduced leakage currents measured for both HfSi_xO_y and ZrSi_xO_y result from the physically thicker 50 Å film as well as from the amorphous structure of the film. Devices that were voltage ramped to hard breakdown consistently showed a breakdown field E_{BD} of $E_{\text{BD}} > 10 \text{ MV/cm}$. The I - V curves in Figs. 10(a) and 10(b) are also seen to be nearly symmetrical, suggesting that transport under both gate and substrate injection may be limited by very similar activation energies.

Figure 11 shows the C - V curves of a 65 Å $\text{Hf}_5\text{Si}_{31}\text{O}_{64}$ film on p^+ Si, deposited at 500 °C, and followed by anneal in forming gas (90% N_2 :10% H_2) at 450 °C for 30 min, with Au electrodes ($A = 1.76 \times 10^{-4} \text{ cm}^2$). The capacitance density measured in accumulation at C_{max} corresponds to $t_{\text{ox}} = 21.2$ Å. Since this film is thicker than that shown in Fig. 9(a), the capacitance density is proportionally lower, but

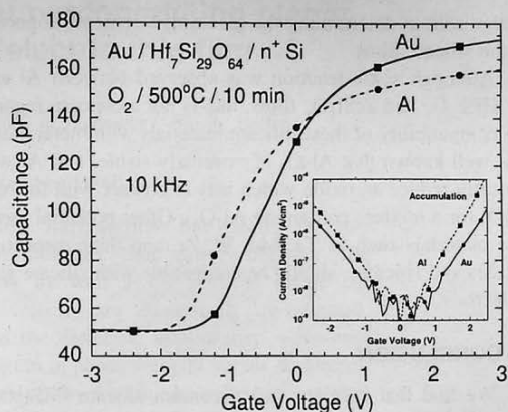


FIG. 12. C - V curves at 10 kHz of a 60 Å $\text{Hf}_7\text{Si}_{29}\text{O}_{64}$ film on n^+ Si, deposited at 400 °C followed by an anneal in O_2 at 500 °C for 10 min, with Au and Al electrodes of equal area. The lower C_{max} value for the Al electrode indicates reaction between the Al and HfSi_xO_y to form a lower- ϵ layer. The larger, negative V_{fb} value for the Al curve results from the lower Al Φ_B value than that of Au, as well as from some C - V stretchout caused by traps in the poor-quality reaction layer. The inset shows the corresponding I - V curves. The higher Φ_B value for Au results in a lower leakage current compared to Al. The reaction layer with Al may also allow slightly higher leakage. The symmetrical Au I - V curves indicate a flatband condition, whereas the lower Al Φ_B value results in asymmetrical silicate barrier heights.

both films exhibit $\epsilon \sim 11$. It is important to note that this film exhibits $V_{\text{fb}} \sim -1$ V on p^+ Si, as expected since the film in Fig. 9(a) showed $V_{\text{fb}} \sim 0$ V on n^+ Si. Some dispersion of the capacitance is visible between 100 kHz and 1 MHz, again indicating the presence of interface traps. No postmetal annealing was done in an attempt to further reduce D_{it} . The leakage current for this film (not shown) was comparable to that shown in Fig. 10, which is about 10^{-6} A/cm^2 at a bias voltage of 1 V in accumulation. The data in Fig. 11 demonstrate that these films can be deposited on heavily doped p^+ Si wafers with high-quality electrical properties.

Au electrodes consistently showed the best electrical behavior for both ZrSi_xO_y and HfSi_xO_y , but Al electrodes were also tested extensively. Reaction between the Al electrodes and the silicate films was nearly always observed, but the resulting electrical properties were still very good. Figure 12 shows the C - V curves at 10 kHz of a 60 Å $\text{Hf}_7\text{Si}_{29}\text{O}_{64}$ film on n^+ Si, deposited at 400 °C followed by an anneal in O_2 at 500 °C for 10 min, with Au and Al electrodes of equal area. The lower C_{max} value for the Al electrode indicates reaction between the Al and HfSi_xO_y to form a lower- ϵ layer. The reaction layer is seen to reduce the C_{max} value by less than 10% of that for Au, which is still high. The larger, negative V_{fb} value for the Al curve results mainly from the lower Al Φ_B value compared to that of Au, as well as from some C - V stretchout caused by traps in the lower- ϵ reaction layer. The inset of Fig. 12 shows the corresponding I - V curves. The higher Φ_B value for Au results in a lower leakage current compared to Al. The reaction layer with Al may also allow slightly higher leakage. The symmetrical Au I - V curves indicate a flatband condition, whereas the lower Al Φ_B value results in asymmetrical silicate barrier heights. Substrate temperature and postannealing conditions will play

a large role in determining the resulting electrical properties of the silicate films.

Although some reaction was observed between Al and the HfSi_xO_y and ZrSi_xO_y films, this is not a concern regarding compatibility of these silicate materials with metal gates. It is well known that Al_2O_3 is extremely stable, and Al will typically reduce an oxide which it is in contact with to form Al_2O_3 (or a mixture containing Al_2O_3). Other potential metal gate materials such as Ta, Mo, W, Zr, and their respective nitrides and silicides, should be compatible with silicate gate dielectrics.

IV. CONCLUSION

We find that hafnium and zirconium silicate (MSi_xO_y , $M=\text{Hf}$ or Zr) gate dielectric films with $\sim 3\text{--}8$ at. % Hf or $2\text{--}5$ at. % Zr exhibit excellent electrical properties and high thermal stability in direct contact with Si. $C\text{--}V$ measurements show an equivalent oxide thickness t_{ox} less than 18 \AA for a 50 \AA $\text{Hf}_6\text{Si}_{29}\text{O}_{65}$ film deposited directly on a Si substrate, which yields a dielectric constant $\epsilon \sim 11$. These physically thick, amorphous films maintain extremely low leakage currents. The silicon oxide-like nature of these films appears to help achieve a high-quality interface with Si, high breakdown field strength, and low hysteresis, while still responding to standard forming gas sinters. More work needs to be done, however, in order to better understand the electron transport mechanisms, and to determine how these films behave in transistors with doped poly-Si gates and full processing treatments.

Since these films were limited to low Hf and Zr concentrations by the source target composition and deposition conditions, films which have compositions closer to stoichiometric MSiO_4 are expected to exhibit a further increased dielectric constant value while maintaining a low leakage current. Obtaining the MSiO_4 stoichiometry should not be necessary, however, especially since it is desirable to maintain an amorphous structure. Any film composition which is somewhat Si rich will be suitable.

ACKNOWLEDGMENTS

The authors are grateful to M. Howell and R. Beavers for outstanding technical support, to J. Julien for XPS measurements, to M. Douglas for ToF SIMS measurements, and to J. Chervinsky for RBS measurements. Thanks go to S. Tang, B. Brar, S. Summerfelt, and L. Colombo for many useful and interesting discussions.

- ¹ H. S. Momose, M. Ono, T. Yoshitomi, T. Ohguro, S.-I. Nakamura, M. Saito, and H. Iwai, *IEEE Trans. Electron Devices* **43**, 1233 (1996).
- ² G. Timp *et al.*, *Tech. Dig. Int. Electron Devices Meet.*, p. 615 (1998).
- ³ J. H. Stathis and D. J. DiMaria, *Tech. Dig. Int. Electron Devices Meet.*, p. 167 (1998).
- ⁴ J. Sapjeta, T. Boone, J. M. Rosamilia, P. J. Silverman, T. W. Sorsch, G. Timp, and B. E. Weir, *Mater. Res. Soc. Symp. Proc.* **477**, 203 (1997).
- ⁵ G. D. Wilk, Y. Wei, H. Edwards, and R. M. Wallace, *Appl. Phys. Lett.* **70**, 2288 (1997).
- ⁶ G. D. Wilk, *Proc. SPIE* **3212**, 42 (1997).
- ⁷ G. Lucovsky, A. Banerjee, B. Hinds, B. Clafflin, K. Koh, and H. Yang, *J. Vac. Sci. Technol. B* **15**, 1074 (1997).
- ⁸ G. D. Wilk and B. Brar, *IEEE Electron Device Lett.* **20**, 132 (1999).
- ⁹ S. V. Hattangady, R. Kraft, D. T. Grider, M. A. Douglas, G. A. Brown, P.

- A. Tiner, J. W. Kuehne, P. E. Nicollian, and M. F. Pas, *Tech. Dig. Int. Electron Devices Meet.*, p. 495 (1996).
- ¹⁰ Y. Wu and G. Lucovsky, *IEEE Electron Device Lett.* **19**, 367 (1998).
- ¹¹ X. W. Wang, Y. Shi, and T. P. Ma, *VLSI Symp. Tech. Dig.*, 109 (1995).
- ¹² A. Chatterjee *et al.*, *Tech. Dig. Int. Electron Devices Meet.*, p. 777 (1998).
- ¹³ I. C. Kizilyalli, R. Y. S. Huang, and P. K. Roy, *IEEE Electron Device Lett.* **19**, 423 (1998).
- ¹⁴ D. Park *et al.*, *IEEE Electron Device Lett.* **19**, 441 (1998).
- ¹⁵ H. F. Luan, B. Z. Wu, L. G. Kang, B. Y. Kim, R. Vrtis, D. Roberts, and D. L. Kwong, *Tech. Dig. Int. Electron Devices Meet.*, p. 609 (1998).
- ¹⁶ B. He, T. Ma, S. A. Campbell, and W. L. Gladfelter, *Tech. Dig. Int. Electron Devices Meet.*, p. 1038 (1998).
- ¹⁷ R. A. McKee, F. J. Walker, and M. F. Chisholm, *Phys. Rev. Lett.* **81**, 3014 (1998).
- ¹⁸ L. Manchanda *et al.*, *Tech. Dig. Int. Electron Devices Meet.*, p. 605 (1998).
- ¹⁹ R. B. van Dover and L. F. Schneemeyer, *IEEE Electron Device Lett.* **19**, 329 (1998).
- ²⁰ G. B. Alers, D. J. Werder, Y. Chabal, H. C. Lu, E. P. Gusev, E. Garfunkel, T. Gustafsson, and R. S. Urdahl, *Appl. Phys. Lett.* **73**, 1517 (1998).
- ²¹ D. C. Gilmer *et al.*, *Chem. Vap. Deposition* **4**, 9 (1998).
- ²² T. Hori, *Gate Dielectrics and MOS ULSIs*, Springer Series in Electronics and Photonics, Vol. 34 (Springer, New York, 1997).
- ²³ M. A. Russack, C. V. Jahnes, and E. P. Katz, *J. Vac. Sci. Technol. A* **7**, 1248 (1989).
- ²⁴ S. Roberts, J. G. Ryan, and D. W. Martin, *Emerging Semiconductor Technology*, ASTM STP 960, edited by D. C. Gupta and P. H. Langer (American Society for Testing Materials, Philadelphia, 1986), p. 137.
- ²⁵ (a) M. Balog, M. Schieber, S. Patai, and M. Michman, *J. Cryst. Growth* **17**, 298 (1972); (b) M. Balog, M. Schieber, M. Michman, and S. Patai, *Thin Solid Films* **41**, 247 (1977); (c) **47**, 109 (1977); (d) *J. Electrochem. Soc.* **126**, 1203 (1979).
- ²⁶ J. Shappir, A. Anis, and I. Pinsky, *IEEE Trans. Electron Devices* **ED-33**, 442 (1986).
- ²⁷ A. Kumar, D. Rajdev, and D. L. Douglass, *J. Am. Chem. Soc.* **55**, 439 (1972).
- ²⁸ R. Beyers, *J. Appl. Phys.* **56**, 147 (1984).
- ²⁹ K. J. Hubbard and D. G. Schlom, *J. Mater. Res.* **11**, 2757 (1996).
- ³⁰ S. Q. Wang and J. W. Mayer, *J. Appl. Phys.* **64**, 4711 (1988).
- ³¹ I. Barin and O. Knacke, *Thermochemical Properties of Inorganic Substances* (Springer, Berlin, 1973).
- ³² L. B. Pankratz, *Thermodynamic Properties of Elements and Oxides* (U.S. Dept. of Interior, Bureau of Mines Bulletin 672, U.S. Govt. Printing Office, Washington, D.C., 1982).
- ³³ S. P. Murarka, *Silicides for VLSI Applications* (Academic, New York, 1983).
- ³⁴ S. Murtaza, J. Hu, S. Unnikrishnan, M. Rodder, and I.-C. Chen, *Proc. SPIE* **3506**, 49 (1998).
- ³⁵ From W. T. Adams, in *Zirconium and Hafnium*, a chapter from Mineral Facts and Problems (U.S. Dept. of Interior, Bureau of Mines Preprint from Bulletin 675, U.S. Govt. Printing Office, Washington, D.C., 1985), pp. 946–947. It is stated that Hf has been used in nuclear reactors as the control rod material, because it has a high thermal neutron capture cross section, and shows little decrease in capture cross section after long periods of radiation exposure. Hafnium also shows high corrosion resistance in hot water, which makes it a low-maintenance material for control rod purposes. Hafnium is therefore not a concern regarding radioactivity.
- ³⁶ W. B. Blumenthal, *The Chemical Behavior of Zirconium* (van Nostrand, Princeton, 1958), pp. 201–219.
- ³⁷ L. Bragg, G. F. Claringbull, and W. H. Taylor, *Crystal Structures of Minerals* (Cornell University Press, Ithaca, 1965), p. 185.
- ³⁸ P. J. Harrop and D. S. Campbell, *Thin Solid Films* **2**, 273 (1968).
- ³⁹ G. D. Wilk and R. M. Wallace, *Appl. Phys. Lett.* **74**, 2854 (1999).
- ⁴⁰ G. D. Wilk and R. M. Wallace (to be published).
- ⁴¹ National Institute of Standards and Technology database.
- ⁴² Z. Lu, J. P. McCaffrey, B. Brar, G. D. Wilk, R. M. Wallace, L. C. Feldman, and S. P. Tay, *Appl. Phys. Lett.* **71**, 2764 (1997).
- ⁴³ Based on $C = \epsilon \epsilon_0 A/t$ for a parallel plate capacitor, where ϵ = relative dielectric constant, $\epsilon_0 = 8.85 \times 10^{-14} \text{ F/cm}$, A = capacitor area, and t = electrical dielectric thickness. Thus $t_{\text{ox}} = 3.9 \epsilon_0 (A/C_{\text{max}})$, and $C/A = 34.5 \text{ fF}/\mu\text{m}^2$ corresponds to $t_{\text{ox}} = 10 \text{ \AA}$.
- ⁴⁴ H. B. Michaelson, *J. Appl. Phys.* **48**, 4729 (1977).
- ⁴⁵ B. Brar, G. D. Wilk, and A. C. Seabaugh, *Appl. Phys. Lett.* **69**, 2728 (1996).