

UNITED STATES PATENT AND TRADEMARK OFFICE

BEFORE THE PATENT TRIAL AND APPEAL BOARD

SONY GROUP CORPORATION,
Petitioner,

v.

VISIONX TECHNOLOGIES, LLC,
Patent Owner.

Case No. TBD
Patent No. 8,035,143

DECLARATION OF MARY K. BOLIN, Ph.D.

Sony Exhibit 1018 Sony v. VisionX

I, Mary K. Bolin, declare as follows:

1. I am Emeritus Professor at the University of Nebraska—Lincoln Libraries. I have held the following positions: Professor and Catalog and Metadata Librarian, Digital Initiatives and Special Collections Department, University of Nebraska—Lincoln Libraries (2015–2020); Professor and Chair, Discovery and Resource Management and Coordinator of Collection Development, University of Nebraska—Lincoln Libraries (2004–2015); Lecturer, San José State University School of Information: Lecturer, (2008–present); Head of the Technical Services Department, University of Idaho Library (1993–2003; promoted to Professor in 1999); Head of the Cataloging Department, University of Idaho Library (1986–1993; promoted to Associate Professor and tenured in 1991); Head of Records Maintenance Section, Cataloging Department, University of Georgia Libraries (1981–1986).

2. Over the course of my work as a librarian, professor, researcher, student research supervisor, and author of numerous scholarly papers and other publications, I have had extensive experience with cataloging records and online library management systems built around Machine-Readable Cataloging (MARC) standards. I also have substantial experience in authenticating printed documents and establishing the date when they were accessible to ordinarily skilled researchers.

3. Attachment A is my full resume.

4. I have been retained by Wolf, Greenfield & Sacks, P.C. to evaluate, authenticate, and establish the dates of public availability of certain documents in the above-captioned IPR proceeding. For my time performing this service, I am being paid my usual hourly fee of \$150 per hour. I have no financial interest in this proceeding, or affiliation with Petitioners. My compensation is not dependent upon the outcome of, or my testimony in, this IPR proceeding.

A. Document of Interest

5. This declaration concerns Garrou, P., Bower, C., and Ramm, P., *Handbook of 3D Integration: Technology and Applications of 3D Integrated Circuits*, Wiley-VCH, 2008. Volume 1 (“**Document 1**”).

B. Methodology

6. I am familiar with many online catalogs, databases, and search engines. In preparing for this declaration, I used authoritative information systems such as WorldCat (<https://www.worldcat.org>) and the online catalog of the Library of Congress (<https://catalog.loc.gov>, “OCLC”), shared research databases such as ResearchGate and CiteSeerX, the online catalog of a number of large research libraries such as the University of Nebraska—Lincoln and the British Library, subscription databases such as IOPScience, and publicly accessible web search engines such as Google Scholar to search for records.

7. I searched for Document 1 using resources such as those listed above. My goal was to find a record (or records) of Document 1 that contained a date indicating when the document was available to the public.

C. Document 1

8. The following are my opinions with respect to the authenticity and public availability of Document 1: Garrou, P., Bower, C., and Ramm, P. (2008). *Handbook of 3D Integration: Technology and Applications of 3D Integrated Circuits*, Wiley-VCH, 2008. Volume 1.

1. Authentication of Document 1

9. I conducted a search for Document 1 in the catalog of the British Library, the result of which is shown in Attachment B. I also conducted an “item display search” for Document 1 in the catalog of the British Library, the result of which is shown in Attachment C. The results of

these searches confirm that Document 1 is in the collection of the British Library and that a publicly-available catalog search shows information concerning Document 1's location in the British Library.

10. I have reviewed Ex. 1016, which contains a scanned copy of a letter from the British Library Research Service in response to a Public Availability Date Request confirming the British Library Public Availability Date (PAD) of Document 1. The letter in Ex. 1016 references an attachment containing a scanned copy of select pages from Document 1 in the British Library that include date-stamps. I understand that those scanned pages are reflected in Ex. 1017. PAD letters like Ex. 1016 are routinely and reasonably relied upon by experts in my field when forming opinions on public availability dates. The British Library's Public Availability Date (PAD) Service is a very well-known and reliable service that provides written confirmation of the date that an item was made available from the British Library. A description of the PAD Service can be found at <https://www.bl.uk/business-and-ip-centre/our-research-service>, which explains that "We will check the date on which the an [sic] item was first made available to British Library users either in our Reading Rooms or through our Document Supply Service and deliver a letter confirming this with a copy of the relevant date stamp."

11. I have reviewed Ex. 1017, which is a scan of the front matter for Document 1 volume 1 from the British Library showing a date stamp, together with the table of contents pages.

12. I have reviewed Ex. 1015, which is a scan of the cover and front matter for Document 1 volume 1, together with the table of contents and pages 157-173 (Chapter 9).

13. Ex. 1017 and Ex. 1015 include identical front matter and table of contents pages, with the only notable difference being the inclusion of handwritten notes and a British Library date stamp on the copyright page contained in Ex. 1017 (at page 2). *Compare* Ex. 1017, page 2 *with*

Ex. 1015, page 3. I have also compared the section headings and page numbers in Chapter 9 in Ex. 1015 with the listed section headings and page numbers in the table of contents pages in Ex. 1015 and Ex. 1017, and found them to be identical.

14. Based on my review of the above, it is my opinion that Ex. 1015 is a true and correct copy of pages from Document 1.

2. Public Availability of Document 1

15. Publisher Wiley Statement

16. Attachment D is the search result page from the Wiley Online Library for Document 1.

17. Document 1 is found in the Wiley Online Library with the statement, “First published: 6 August 2008.” Wiley is a well-known and reputable publisher.

18. British Library Date Stamp and Letter

19. I understand from the PAD letter from the British Library (Ex. 1016) that “According to our records, these items (Volumes 1 & 2) were receipted by The British Library for Volume 1 receipted 15th August 2008 and Volume 2 receipted 10th September 2008, and they would have been available for public use from these dates.”

20. I understand from the PAD letter Ex. 1016 that Ex. 1017 contains a date stamp indicating the date of availability of Volume 1 at the British Library. Consistent with the statement in Ex. 1016, there is a date stamp appearing on page 2 of Ex. 1017 reflecting August 15, 2008 as the date of public availability for Document 1.

21. Actual Usage

22. Availability and actual usage of a printed document are reflected by subsequent research papers making reference to it. My research, using resources such as Google Scholar and IOPScience, has identified at least one article that cited Document 1.

23. Attachment E is the search result from IOPScience showing search results for the article Knoops et al. (2008) Deposition of TiN and TaN by remote plasma ALD for Cu and Li diffusion barrier applications. *Journal of the Electrochemical Society*, 155(12), G287-G294 that cites Document 1. Ex. 1019 is a PDF copy downloaded from IOPScience for the Knoops et al. article. Attachment F is a screenshot of the PDF properties of Ex. 1019.

24. Document 1 is cited by the Knoops et al. article as reference [1]. Both the IOPScience search results page (Attachment E) and the PDF copy (Ex. 1019) for Knoops et al. include a statement, “Published 10 October 2008.” The PDF properties of Ex. 1019, which indicate that the PDF file was created on October 10, 2008, are consistent with an October 10, 2008, publication date.

25. In sum, Document 1 was added to the British Library collection on August 15, 2008, appears in the Wiley Online Library with a publication date of August 6, 2008, and was cited by an article in the IOPScience database with publication date of October 10, 2008. Based on these facts, it is my opinion that Document 1 was publicly available in August 2008—and certainly no later than October 2008, when the Knoops et al. article was published—and could have been located by a skilled researcher.

* * *

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine,

imprisonment, or both, under Section 1001 of Title 18 of the U.S. Code. I state under penalty of perjury under the laws of the United States of America that the foregoing is true and correct.

Executed this December 12, 2022, in Kansas City, Missouri.

A handwritten signature in black ink, appearing to read "Mary K. Bolin", is written over a light gray, textured rectangular background.

Mary K. Bolin

ATTACHMENT A

Mary K. Bolin, PhD
2433 U Street
Lincoln, Nebraska 68503
mary@marykbolin.com

Mary K. Bolin, PhD

Professor Emeritus
University Libraries
University of Nebraska—Lincoln
mbolin2@unl.edu

Lecturer,
School of Information
San José State University
mary.bolin@sjsu.edu

EDUCATION

PhD, Educational Studies (Educational Leadership and Higher Education), 2007, University of Nebraska

Dissertation: *A Typology and Discourse Analysis of the Status and Appointments of Librarians at Land Grant Universities* (available at digitalcommons.unl.edu)

MA, English, 1999, University of Idaho

Thesis: *Grace: A Contrastive Analysis of a Biblical Semantic Field* (available at digitalcommons.unl.edu)

MSLS, 1981, University of Kentucky

BA, Linguistics, 1976, University of Nebraska—Lincoln

WORK EXPERIENCE

Center for Digital Research in the Humanities. Fellow, 2019- Emeritus, 2020-

University of Nebraska--Lincoln Libraries: Professor and Catalog and Metadata Librarian, Digital Initiatives and Special Collections, 2015-2020. Emeritus, 2020-

University of Nebraska—Lincoln Libraries: Professor and Chair, Discovery and Resource Management, 2004-2015; Coordinator of Collection Development, 2012-2015

University of Idaho Library: Head, Technical Services Department, 1993-2003. Promoted to Professor in 1999

University of Idaho Library: Head, Cataloging Department, 1986-1993. Promoted to Associate Professor and tenured, 1991

University of Georgia Libraries: Head, Records Maintenance Section, Cataloging Department, 1981-1986

Teaching:

San José State University School of Information:

LIBR 281, Metadata. 2009-

LIBR 248, Introduction to Cataloging and Classification. 2013-

LIBR 202, Information Retrieval. 2008-2013

Associate Coordinator, Gateway PhD program, San Jose State University, 2021-

American Library Association

Cataloging for Non-Catalogers, Online Continuing Education Course, 2017-

Intermediate Cataloging for Non-Catalogers, Online Continuing Education Course, 2018-

Lyrasis

Webinar on BibFrame, taught twice a year, 2020-

Quick and Clean Cataloging, Parts 1, 2, and 3. 2022-

Independent Study in Idaho

Library Science C415, Technical Services for Small Libraries, 2004-2013

Library Science C416, Library Services to Rural Libraries, 2004-2013

Library Science C422, Use of the School Library, 1999-2013

Library Science C425/525, Organization and Management of Small Libraries,
1988-2013

Library Science C427, Library or Media Center Practicum, 1995-2013

Gateway PhD Program (San Jose State University and Queensland University of Technology).
SJSU supervisor for two PhD students, 2015-

Gateway PhD Program (San Jose State University and Manchester Metropolitan University).
Associate Coordinator, 2021-

Consulting

Expert witness for multiple attorneys employed by Wolf, Greenfield & Sacks, P.C.,
Hughes Hubbard & Reed LLP, and other firms. 2017-

Editing

Language and academic editing for [EditSprings](#), a service for international scholars, 2020-

SCHOLARSHIP

Refereed Publications:

(Publications available from [digitalcommons.unl.edu](#))

Bolin, Mary K. (2022). "Academic Libraries and Writing Centers: Collaborations at US Public Research Universities." *School of Information Student Research Journal*, 11(2). Retrieved from <https://scholarworks.sjsu.edu/ischoolsrj/vol11/iss2/2>

Bolin, Mary K. (Forthcoming 2022). *Refocusing Academic Libraries through Learning and Discourse: The Idea of a Library*. Oxford, UK: Chandos/Elsevier.

Bolin, Mary K. (2022). "Metadata, Catalog Systems, Linked Data, and the Evolving ILS." In: Sandra Hirsh (Ed.), *Information Services Today: An Introduction*. 3rd ed. New York: Rowman and Littlefield.

Pytlík Zillig, Brian, and Mary K. Bolin. (Forthcoming) "Visualization of Semantic Primes in Texts from Early Modern English Drama." *Journal of the Japanese Association for the Digital Humanities*.

Wintermute, Harriet E., and Bolin, Mary K. (2018). "Metadata Generators for Backlog Reduction: Metadata Maker Streamlines Cataloging and Facilitates Transition. *Technical Services Quarterly* 35(2) doi: <https://doi.org/10.1080/07317131.2018.1422879>

Bolin, Mary K. (2018). "Metadata, Catalog Systems, Linked Data, and the Evolving ILS." In: Sandra Hirsh (Ed.), *Information Services Today: An Introduction*. 2nd ed. New York: Rowman and Littlefield.

Bolin Mary K. (2017). *The 21-century Academic Library: Global Patterns of Organization and Discourse*. Oxford: Chandos Publishing. (Chandos Information Professional Series)

Bolin, Mary K. (2017). Linguistics and LIS: A Research Agenda." *SLIS Student Research Journal*, 7:1.

Retrieved from <http://scholarworks.sjsu.edu/slissrj/vol7/iss1/2>

Bolin, Mary K. (2014). "Open Access Web Resources for Library Continuing Education and Training." In S. Hines (Ed.), *Revolutionizing the Development of Library and Information Professionals: Planning for the Future* (pp. 107- 124). Hershey, PA: . doi:10.4018/978-1-4666-4675-9.ch008.

Bolin, Mary K. (2014). "The Language of Academic Librarianship: The Discourse of Promotion and Tenure. " *Advances in Library Administration and Organization* 32.

Bolin, Mary K. "Librarian Status at US Research Universities: Extending the Typology." *Journal of Academic Librarianship* 34:4 (September 2008)

Bolin, Mary K. "A Typology of Librarian Status at Land Grant Universities." *Journal of Academic Librarianship*, 34: 3 (May 2008)220:230.

Bolin, Mary K. "The Library and the Computer Center: Organizational Patterns at Land Grant Universities." *Journal of Academic Librarianship*, 31:1 (2005)

Eckwright, Gail Z. and Mary K. Bolin. "The Hybrid Librarian: The Affinity of Collection Management with Technical Services and the Organizational Benefits of an Individualized Assignment." *Journal of Academic Librarianship*, 27:6 (2001)452:457.

Bolin, Mary K. "Catalog Design, Catalog Maintenance, Catalog Governance," *Library Collections, Acquisitions, and Technical Services*. 24: (2000)53-63.

Bolin, Mary K. "The Collegial Environment and the Functional Organization," *Journal of Library Administration*. 29:2(1999):49-61.

Bolin, Mary K. "Cataloging Environmental Impact Statements and Related Documents," *Resource Sharing and Library Networks*. 14:1(1999): 21-40.

Bolin, Mary K. "Waiting for the Electrician or Someone like Him: Client-Centered Technical Services" Proceedings of the Association of College and Research Libraries National Conference, Nashville, April 1997.

< http://www.ala.org/Content/ContentGroups/ACRL1/Nashville_1997_Papers/Bolin.htm >

Grants:

Electronic Theses and Dissertations. Seed Grant from University of Idaho Office of Research, 2002. Co PI with Gail Z. Eckwright. \$6500.

Interoperability of Metadata for Thematic Research Collections. Grant to the Center for Digital Research in the Humanities from the Institute of Museum and Library Services 2005-2008. Project Team Member.

http://unlcms.unl.edu/cas/center-for-digital-research-in-the-humanities/projects/pages/iom_files/IOM_Final_Narrative_Report_July_2008.pdf

Other Publications:

Library Philosophy & Practice. Peer-reviewed electronic library science journal. Mary K. Bolin and Gail Z. Eckwright, founders and editors. <http://digitalcommons.unl.edu/libphilprac>

Library Science C415, Technical Services for Small Libraries, through Independent Study in Idaho. 2004.

Library Science C416, Library Services to Rural Libraries, through Independent Study in Idaho. 2004.

Library Science C422, Use of the School Library, through Independent Study in Idaho. Revised 1999.

Library Science C425/525, Organization and Management of Small Libraries through Independent Study in Idaho. Revised 2005.

Library Science C427, Library or Media Center Practicum, Independent Study in Idaho. Revised 1999.

Presentations:

Bolin, Mary K. "BibFrame and the MARC Cataloging Environment: an Introduction." Lyrisis Webinar, June 16, 2020, August 17, 2021.. Recording available <http://lyrisis.adobeconnect.com/paufo9e0dm30/>

Pytlik Zillig, Brian, and Mary K. Bolin. "A Little More than Kin, a Little Less than Kind": the Semantic Field Grace in Early Modern English" Poster Session, Text Encoding Initiative Meeting, Graz, Austria, September 18, 2019

Pytlik Zillig, Brian, and Mary K. Bolin. "Shakespeare and the Enumeration of Semantic Primes." Research Paper Presentation, Text Encoding Initiative Meeting, Tokyo, Japan, September 13, 2018

"Library Philosophy and Practice: Creating and Maintaining an Open-Access E-Journal," Presentation to UNCL meeting (libraries at campuses of the University of Nebraska), Lincoln, Nebraska, March 20, 2008.

Presentation to "Thinking outside the Borders" participants on the open-access electronic journal Library Philosophy and Practice and its role in the international library community. University of Nebraska—Lincoln Libraries, October 24, 2007

Panel discussion on open access electronic journals. GWLA directors' meeting. Linda K. Hall Library, Kansas City, Missouri. April 2007.

"Waiting for the Electrician or Someone Like Him: Client-Centered Technical Services." Association of College and Research Libraries National Conference, Nashville, April 5, 1997.

" 'Some Problems of an Editor': the Idaho Librarian from Manuscript to Published Issue," Joint Annual Conference of the Idaho Library Association and the Washington Library Association, Spokane, Washington, April 6, 1995.

"Automating Idaho's Libraries: a Historical Perspective." Idaho Library Association Annual Conference, Idaho Falls, October 4, 1990.

"Small Library Management." Idaho Library Association Spring Conference, Lewiston, Idaho, May 13, 1989.

"No More 'Good Workers': Excellence and Academic Library Classified Staff." Association of College and Research Libraries 5th Annual Conference, Cincinnati, April 7, 1989.

"Communication to and from Cataloging Departments." Heads of Cataloging Discussion Group, American Library Association Midwinter Meeting, San Antonio, January 1988.

Discussion Leader at the LAMA (Library Administration and Management) Management Exchange. American Library Association Annual Meeting, San Francisco, June 1987.

"Staff Turnover." Heads of Cataloging Discussion Group, American Library Association Midwinter Meeting, Chicago, January 1987.

SELECTED PROFESSIONAL SERVICE

Reviewer. *Resources for College Libraries*. Linguistics bibliography, Spring 2020.

Peer reviewer for ALISE National Conference presentations, Spring 2020.

Peer reviewer for *Journal of Academic Librarianship*, 2012-

Peer reviewer for refereed journal, *Western Nigerian Journal of Medical Sciences* (<http://www.wnjms.org/>), a publication of Ladoke Akintola University of Technology (LAUTECH) Teaching Hospital, 2008-

PhD Reviewer for students from Aligarh Muslim University, India, 2010-

Outside reviewer for numerous library faculty promotion and tenure cases in US universities.

University of Nebraska--Lincoln

Chair, University Libraries Faculty, 2018

Faculty Senate Academic Rights and Responsibilities Committee, 2016- Chair, 2018-19

Faculty Senate – 2004-2008; 2008-2011

Faculty Senate Executive Committee 2004-2008

Academic Planning Committee (APC), 2005-2008; Vice Chair, 2006-2007; Chair, 2007-2008

Aesthetic Review Committee 2006-2007

APC monitor for academic program reviews: Department of Political Science, 2005;
Department of Educational Psychology 2006
Pacific Northwest Library Association:

Editor, *PNLA Quarterly*, December 2002-December 2013

Idaho Library Association:

Editor, *The Idaho Librarian*, September 1990-January 1996

ATTACHMENT B

Explore the British Library

Explore HomeFeedbackBasketRequest Other ItemsMy Reading Room RequestsHelp

Main catalogueAvailable online (beta)Our websiteExplore Further

garrou handbook of 3d integrationEverything in this catalogueAdvanced Search

[Back to results list](#)

Handbook of 3D integration : technology and applications of 3D integrated circuits / edited by Philip Garrou, Christopher Bower and Peter Ramm.
Weinheim : Wiley-VCH, 2008.

DetailsI want this

Actions

Title: Handbook of 3D integration : technology and applications of 3D integrated circuits / edited by Philip Garrou, Christopher Bower and Peter Ramm.

Contributor: [Philip E Garrou](#);
[Christopher Andrew Bower](#);
[Peter Ramm](#)

Subjects: [Integrated circuits](#); [Integrated circuits -- Design and construction](#);
[Semiconductor wafers](#); [Three-dimensional imaging](#);
[Dewey: 621.3815](#)

Rights: Terms governing use: Current Copyright Fee: GBP32.00

Publication Details: Weinheim : Wiley-VCH, 2008.

Language: English

Identifier: ISBN 9783527320349 (set) : £135.00; BNB GBA8A2148; System number: 014470978

Notes: Bibliography note: Includes bibliographical references and index.

Physical Description: 2 v. : ill. (some col.) ; 25 cm.

Obsolete shelfmark: (B) 621.3815

Shelfmark(s): Document Supply m08/.29671 vol. 2
Document Supply m08/.29670 vol. 1
Science, Technology & Business (B) 621.3815 v.2
General Reference Collection YC.2016.a.12928

UIN: BLL01014470978

Links

- [Item Holdings](#)
- [View record in Library Hub Discover](#)
- [View record in WorldCat®](#)
- [Report Catalogue Error](#)
- [MARC display](#)

[Back to results list](#)

[Previous Result](#) 4

ATTACHMENT C



EXPLORE THE BRITISH LIBRARY

Item Holdings

[Back](#)

Handbook of 3D integration :technology and applications of 3D integrated circuits /edited by Philip Garrou, Christopher Bower and Peter Ramm..

Weinheim : Wiley-VCH, 2008..

2 v. : ill. (some col.) ; 25 cm..

Collection;Shelfmk General Reference Collection ; YC.2016.a.12928

Collection;Shelfmk Lending Collection ; m08/.29671 ; vol. 2

Collection;Shelfmk Lending Collection ; m08/.29670 ; vol. 1

Collection;Shelfmk Science Technology and Industr (B) ; 621.3815 ; v.2

For serials, the holdings data below may not be complete. If the issue you require was published before serial holdings were individually recorded it may still be held. The extent of the Library's holdings may be summarised in a holdings note above.

Select year Select volume Select Collection

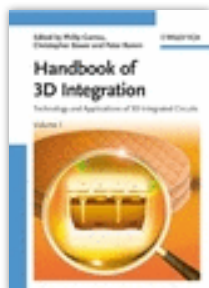
Description	Item status	Collection	Sub-coll.	Shelfmark	Note
Vol. 2	Available	Science Technology and Industr		(B) 621.3815 v.2	
Vol. 2	Available	Lending Collection		m08/.29671 vol. 2	
Vol. 1	Available	General Reference Collection		YC.2016.a.12928	
Vol. 1	Available	Lending Collection		m08/.29670 vol. 1	

[Accessibility](#) [Terms of use](#)

All text is © British Library Board and is available under a [CC-BY](#) Licence except where otherwise stated

P2

ATTACHMENT D



Handbook of 3D Integration: Technology and Applications of 3D Integrated Circuits

Editor(s): Dr. Philip Garrou, Dr. Christopher Bower, Dr. Peter Ramm

First published: 6 August 2008

Print ISBN: 9783527320349 | Online ISBN: 9783527623051 | DOI: 10.1002/9783527623051

Copyright © 2008 Wiley-VCH Verlag GmbH & Co. KGaA

About this book

The first encompassing treatise of this new, but very important field puts the known physical limitations for classic 2D electronics into perspective with the requirements for further electronics developments and market necessities. This two-volume handbook presents 3D solutions to the feature density problem, addressing all important issues, such as wafer processing, die bonding, packaging technology, and thermal aspects.

 [View and download full book](#)

Table of Contents

[” Export Citation\(s\)](#)

 [Free Access](#)

[Front Matter \(Pages: I-XXVI\)](#)

[Summary](#) | [PDF](#) | [Request permissions](#)

CHAPTER 1

[Full Access](#)

Introduction to 3D Integration (Pages: 1-11)

Dr. Philip Garrou

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 2

[Full Access](#)

Drivers for 3D Integration (Pages: 13-24)

Dr. Philip Garrou, Susan Vitkavage, Sitaram Arkalgud

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 3

[Full Access](#)

Overview of 3D Integration Process Technology (Pages: 25-44)

Dr. Philip Garrou, Dr. Christopher Bower

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 4

[Full Access](#)

Deep Reactive Ion Etching of Through Silicon Vias (Pages: 45-91)

Fred Roozeboom, Michiel A. Blauw, Yann Lamy, Eric van Grunsven, Wouter Dekkers, Jan F. Verhoeven, Eric(F.) van den Heuvel, Emile van der Drift, Erwin (W. M. M.) Kessels, Richard (M. C. M.) van de Sanden

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 5

[Full Access](#)

Laser Ablation (Pages: 93-105)

Wei-Chung Lo, S. M. Chang

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 6

[Full Access](#)

SiO₂ (Pages: 107-120)

Robert Wieland

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 7

[Full Access](#)

Insulation – Organic Dielectrics (Pages: 121-131)

Dr. Philip Garrou, Dr. Christopher Bower

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 8

[Full Access](#)

Copper Plating (Pages: 133-156)

Tom Ritzdorf, Rozalia Beica, Charles Sharbono

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 9

[Full Access](#)

Metallization by Chemical Vapor Deposition of W and Cu (Pages: 157-173)

Armin Klumpp, Robert Wieland, Ramona Ecke, Stefan E. Schulz

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 10

[Full Access](#)

Fabrication, Processing and Singulation of Thin Wafers (Pages: 175-208)

Werner Kröninger

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 11

[!\[\]\(90c859a17dbc6c3879e6b0c04b61632c_img.jpg\) Full Access](#)**Overview of Bonding Technologies for 3D Integration (Pages: 209-221)**

Jean-Pierre Joly

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 12

[!\[\]\(11180f88349a0f55a115986a3613acf7_img.jpg\) Full Access](#)**Chip-to-Wafer and Wafer-to-Wafer Integration Schemes (Pages: 223-248)**

Thorsten Matthias, Stefan Pargfrieder, Markus Wimplinger, Paul Lindner

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 13

[!\[\]\(eba903ee4dc5f81044c5c13ca9966076_img.jpg\) Full Access](#)**Polymer Adhesive Bonding Technology (Pages: 249-259)**

James Jian-Qiang Lu, Tim S. Cale, Ronald J. Gutmann

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 14

[!\[\]\(3e20e1de1ec46120aff11818eeebf90e_img.jpg\) Full Access](#)**Bonding with Intermetallic Compounds (Pages: 261-269)**

Armin Klumpp

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 15

[!\[\]\(28944797265a0fe37c5b57b30aabff7f_img.jpg\) Full Access](#)**Commercial Activity (Pages: 271-287)**

Dr. Philip Garrou

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 16

[Full Access](#)

Wafer-Level 3D System Integration (Pages: 289-318)

Dr. Peter Ramm, M. Jürgen Wolf, Bernhard Wunderle

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 17

[Full Access](#)

Interconnect Process at the University of Arkansas (Pages: 319-337)

Susan Burkett, Leonard Schaper

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 18

[Full Access](#)

Vertical Interconnection by ASET (Pages: 339-373)

Kenji Takahashi, Kazumasa Tanida

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 19

[Full Access](#)

3D Integration at CEA-LETI (Pages: 375-392)

Barbara Charlet, Lèa Di Cioccio, Patrick Leduc, David Henry

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 20

[Full Access](#)

Lincoln Laboratory's 3D Circuit Integration Technology (Pages: 393-411)

James Burns, Brian Aull, Robert Berger, Nisha Checka, Chang-Lee Chen, Chenson Chen, Pascale Gouker, Craig Keast, Jeffrey Knecht, Antonio Soares, Vyshnavi Suntharalingam, Brian Tyrrell, Keith Warner, Bruce Wheeler, Peter Wyatt, Donna Yost

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 21

[Full Access](#)

3D Integration Technologies at IMEC (Pages: 413-430)

Eric Beyne

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 22

[Full Access](#)

Fabrication Using Copper Thermo-Compression Bonding at MIT (Pages: 431-446)

Chuan Seng Tan, Andy Fan, Rafael Reif

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 23

[Full Access](#)

Rensselaer 3D Integration Processes (Pages: 447-462)

James Jian-Qiang. Lu, Tim S. Cale, Ronald J. Gutmann

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 24

[Full Access](#)

3D Integration at Tezzaron Semiconductor Corporation (Pages: 463-486)

Robert Patti

[Summary](#) | [PDF](#) | [Request permissions](#)

CHAPTER 25

[Full Access](#)

3D Integration at Ziptronix, Inc. (Pages: 487-503)

Paul Enquist

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 26

[Full Access](#)

3D Integration ZyCube (Pages: 505-515)

Makoto Motoyoshi

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 27

[Full Access](#)

Design for 3D Integration at North Carolina State University (Pages: 517-527)

Paul D. Franzon

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 28

[Full Access](#)

Modeling Approaches and Design Methods for 3D System Design (Pages: 529-574)

Peter Schneider, Günter Elst

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 29

[Full Access](#)

Multiproject Circuit Design and Layout in Lincoln Laboratory's 3D Technology (Pages: 575-582)

James Burns, Robert Berger, Nisha Checka, Craig Keast, Brian Tyrrell, Bruce Wheeler

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 30

[Full Access](#)

Computer-Aided Design for 3D Circuits at the University of Minnesota (Pages: 583-597)

Sachin S. Sapatnekar

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 31

[Full Access](#)

Electrical Performance of 3D Circuits (Pages: 599-621)

Arne Heitmann, Ulrich Ramacher

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 32

[Full Access](#)

Testing of 3D Circuits (Pages: 623-633)

T. M. Mak

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 33

[Full Access](#)

Thermal Management of Vertically Integrated Packages (Pages: 635-649)

Thomas Brunschwiler, Bruno Michel

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 34

[Full Access](#)

3D and Microprocessors (Pages: 651-674)

Pat Morrow, Sriram Muthukumar

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 35

[Full Access](#)

3D Memories (Pages: 675-688)

Mark Tuttle

[Summary](#) | [PDF](#) | [Request permissions](#)

CHAPTER 36

[Full Access](#)

3D Read-Out Integrated Circuits for Advanced Sensor Arrays (Pages: 689-701)

Dr. Christopher Bower

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 37

[Full Access](#)**Power Devices (Pages: 703-721)**

Marc de Samber, Eric van Grunsven, David Heyes

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)

CHAPTER 38

[Full Access](#)**Wireless Sensor Systems – The e-CUBES Project (Pages: 723-746)**

Adrian M. Ionescu, Eric Beyne, Thierry Hilt, Thomas Herndl, Pierre Nicole, Mihai Sanduleanu, Anton Sauer, Herbert Shea, Maaïke Taklo, Co Van Veen, Josef Weber, Werner Weber, Jürgen M. Wolf, Peter Ramm

[Summary](#) | [PDF](#) | [References](#) | [Request permissions](#)[Free Access](#)**Conclusions (Pages: 747-748)**[PDF](#) | [Request permissions](#)[Free Access](#)**Index (Pages: 749-773)**[First Page](#) | [PDF](#) | [Request permissions](#)

About Wiley Online Library

[Privacy Policy](#)[Terms of Use](#)[About Cookies](#)[Manage Cookies](#)[Accessibility](#)[Wiley Research DE&I Statement and Publishing Policies](#)[Developing World Access](#)[Help & Support](#)[Contact Us](#)

Training and Support
DMCA & Reporting Piracy
Opportunities

Subscription Agents
Advertisers & Corporate Partners

Connect with Wiley

The Wiley Network
Wiley Press Room

Copyright © 1999-2022 John Wiley & Sons, Inc. All rights reserved

ATTACHMENT E

Deposition of TiN and TaN by Remote Plasma ALD for Cu and Li Diffusion Barrier Applications

H. C.M. Knoop^{5,7,1,2}, L. Baggetto², E. Langereis^{6,7,2}, M. C.M. van de Sanden², J. H. Klootwijk³, F. Roozeboom^{6,2,4}, R. A.H. Niessen³, P. H.L. Notten^{6,2,3} and W. M.M. Kessels^{6,7,2}

Published 10 October 2008 • © 2008 ECS - The Electrochemical Society

Journal of The Electrochemical Society, Volume 155, Number 12

Citation H. C.M. Knoop *et al* 2008 *J. Electrochem. Soc.* **155** G287

DOI 10.1149/1.2988651

¹ Materials Innovation Institute M2i, 2600 GA Delft, The Netherlands

² Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

³ Philips Research, 5656 AE Eindhoven, The Netherlands

⁴ NXP-TSMC Research Center, 5656 AE Eindhoven, The Netherlands

⁵ Electrochemical Society Student Member.

⁶ Electrochemical Society Active Member.

⁷ E-mail: h.c.m.knoop@tue.nl; w.m.m.kessels@tue.nl

1. Received 22 July 2008

2. Revised 2 September 2008

3. Published 10 October 2008

Buy this article in print

 Journal RSS

Sign up for new issue notifications

Create citation alert

PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.

Abstract

TaN and TiN films were deposited by remote plasma atomic layer deposition (ALD) using the combinations of $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ precursor with H_2 plasma and TiCl_4 precursor with $\text{H}_2 - \text{N}_2$ plasma, respectively. Both the TaN and TiN films had a cubic phase composition with a relatively low resistivity (TaN: $380 \mu\Omega \text{ cm}$; TiN: $150 \mu\Omega \text{ cm}$). Dissimilar from the TiN properties, the material properties of the TaN films were found to depend strongly on the plasma exposure time. Preliminary tests on planar substrates were carried out revealing the potential of the TaN and TiN films as Cu and Li diffusion barriers in through-silicon via and silicon-integrated thin-film battery applications, respectively. For the specific films studied, it was found that TiN showed better barrier properties than TaN for both application areas. The TiN films were an effective barrier to Cu diffusion and had no Cu diffusion for anneal temperatures up to 700°C . The TiN films showed low Li intercalation during electrochemical charging and discharging.

Export citation and abstract

[BibTeX](#)

[RIS](#)

◀ **Previous** article in issue

Next article in issue ▶

Diffusion barrier layers are of key importance to ensure device lifetime and functionality of various components. One area placing stringent demands on the barrier layer is Cu interconnect technology. Here, barrier layers are needed to prevent Cu diffusion into the silicon substrate. Because of scaling down of feature sizes, these films need to be thin (~ 5 to 10 nm) and deposited conformally in features with increasingly higher aspect ratios. Furthermore, the films need to be conductive to maintain sufficient electrical connection to the underlying metallization layer.

Copper diffusion barriers are also needed in the emerging field of three-dimensional (3D) stacked die integration. Here, copper-filled through-silicon vias (TSVs) offer a solution to the "twisting crisis" in next-generation semiconductor devices.¹⁻⁴ 3D integration and more, see our Privacy and Cookies policy.

PDF

Help



consequently, Cu diffusion barriers are also of strategic relevance for the "More than Moore" approach in which several functionalities and components (computing, processing, storage, transmitting, sensing, etc.) are combined in, for example, "System-in-Package (SiP)" devices.⁵

A development being part of the "More than Moore" approach is research toward 3D integrated solid-state thin-film batteries.^{6–8} These batteries have the potential to provide the high-density storage capacity required for future miniaturized autonomous wireless devices or as a backup power supply in circuits.^{6, 7} The batteries are based on Li ions as charge carriers and high aspect ratio structures in silicon to obtain high storage densities. The battery stack consists of several functional layers (diffusion barrier layer, anode, electrolyte, cathode, current collector) deposited conformally in these 3D structures. Because silicon easily takes up elemental Li, it is an attractive anode material. However, to prevent the loss of Li from the Si anode to the underlying Si substrate while still providing an electrical connection to the anode layer, a conductive and conformal Li diffusion barrier film is required in-between.^{6, 7}

As Cu diffusion barrier materials, mainly refractory metallic systems (Ti, Ta, W, Mo, Cr, etc. and their nitrides) are used due to their characteristic chemical inertness and low diffusion rate related to their high melting points.^{9, 10} Furthermore, because of the relatively low resistivity of these materials they can be directly used as metal electrodes in capacitor structures and as metal gate electrodes for complementary metal oxide semiconductor.^{11, 12} Among these materials, TaN and TiN have been considered most often and these materials are known to be good diffusion barriers, especially for Cu.^{9, 10, 12–14} Both sputtered TaN and TiN have been used as a diffusion barrier for TSV experiments.^{4, 15} Note, that the adhesion of Cu on TiN might not be sufficient for the small feature sizes in the more traditional interconnect technology. Nevertheless TiN is considered to be a good candidate for the relatively large vias used in 3D integration.^{1, 4}

In this article, we report on TaN and TiN films deposited with remote plasma atomic layer deposition (ALD). In principle, this technique is capable of depositing high-quality films with a good conformality in high aspect ratio structures.^{12, 16–19} Because the microstructure and the composition of the films could have a large influence on the diffusion barrier properties,^{14, 17, 20–22} we have studied the material properties of the deposited TaN and TiN films for various deposition conditions. In addition, preliminary diffusion barrier experiments were carried out

PDF
Help

on planar wafers to test the performance of TaN and TiN films as Cu and Li diffusion barriers in future SiP applications. Furthermore, by comparing the diffusion barrier properties for both Cu and Li, more insight into the barrier characteristics of TaN and TiN has been obtained.

Experimental

Remote plasma ALD reactors

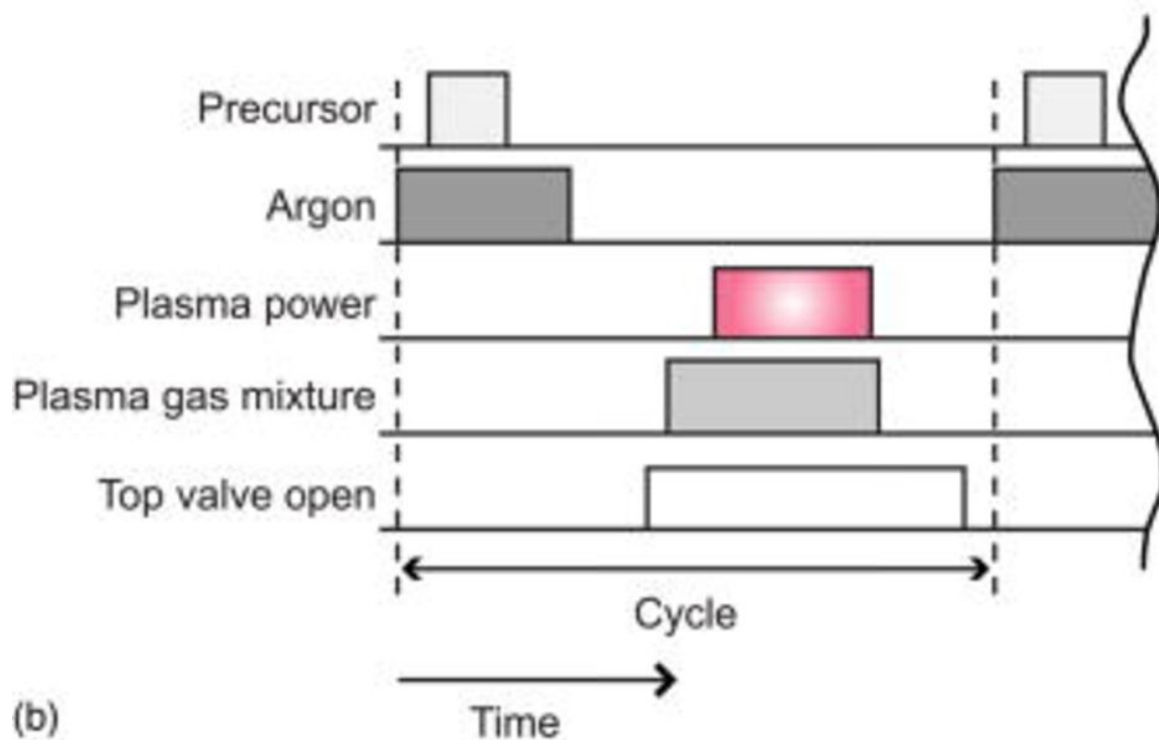
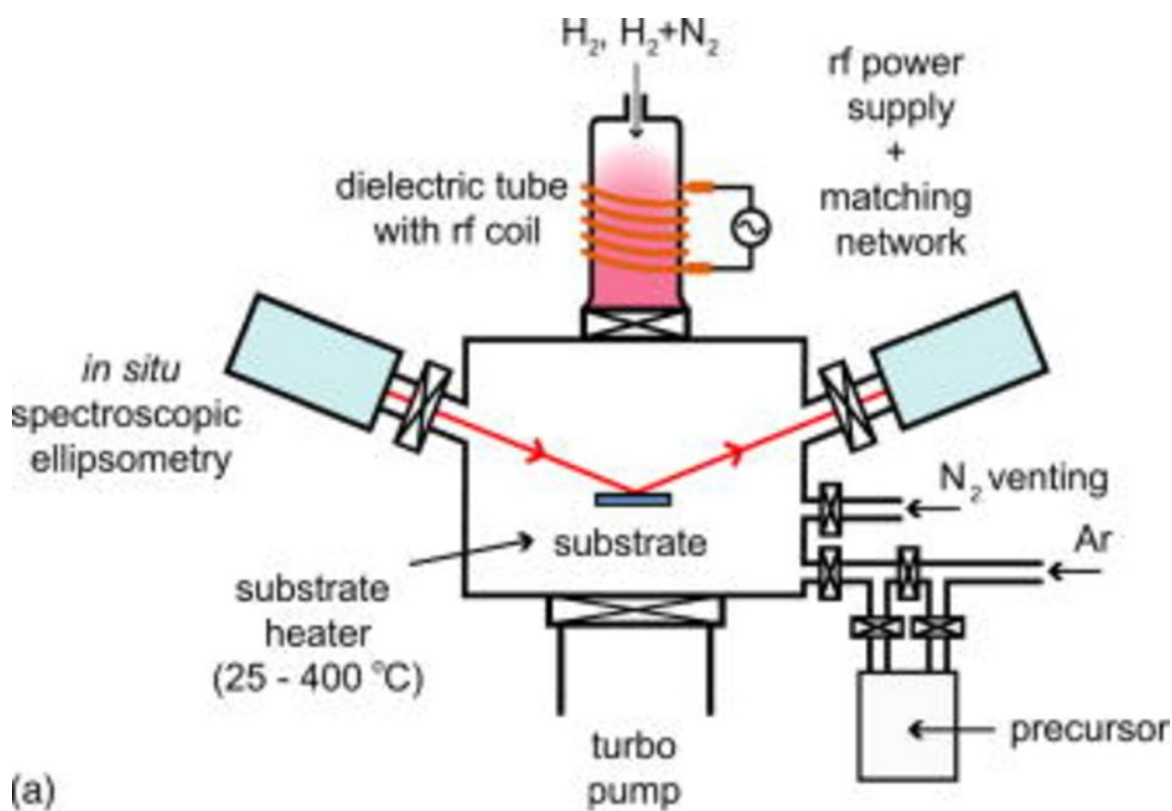
The TaN and TiN films investigated and used in the barrier experiments were deposited using two remote plasma ALD reactors. The TaN films were deposited using the homebuilt ALD-I reactor as described extensively by Langereis et al.²³ The TiN films in this work were deposited using the Oxford Instruments FlexAL reactor, and this process is described by Heil et al.²⁴ In this work, we describe the deposition of both materials and report on the Cu and Li diffusion barrier properties on planar film stacks.

Both ALD reactors have the same basic configuration as schematically represented in Fig. 1a. The reactors consisted of a deposition chamber, a pump unit, an inductively coupled plasma source, and a precursor dosing system. The pump unit and plasma source were connected to the deposition chamber through gate valves. The chamber was pumped by a combination of a turbomolecular pump and a rotary pump reaching a base pressure of $< 10^{-5}$ Torr by overnight pumping. The ALD-I reactor was an open-load reactor that could handle wafers with a diameter up to 100 mm. The FlexAL reactor could handle wafers with diameters up to 200 mm, and these wafers were loaded through a load lock. Unlike the ALD-I reactor, the FlexAL reactor had a higher maximum power setting for the plasma source (600 W instead of 100 W) and was also equipped with mass flow controllers and an automated pressure control valve.

PDF

Help





PDF
Help

Figure 1. (a) A schematic overview of the basic configuration of the remote plasma ALD reactors. In addition to the different reactor components, the in situ spectroscopic ellipsometer is also shown. (b) A schematic of a typical remote plasma ALD cycle for the deposition of conductive thin films.

Figure 1b schematically shows a typical ALD cycle used for both processes. The cycle began with the precursor dosage. For the TaN process $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ (pentakis(dimethylamino)tantalum, PDMAT) precursor was heated to 75°C , and an Ar flow was used to transport the $\text{Ta}[\text{N}(\text{CH}_3)_2]_5$ vapor into the chamber by bubbling. A dosing time of 5 s was used to obtain saturation. For TiN deposition, TiCl_4 was dosed using a fast switch valve (minimum switch time was 10 ms). Because of the high vapor pressure of TiCl_4 , only a short dosage time of 40 ms was required to achieve saturation while keeping the TiCl_4 at 30°C . After purging with Ar, the gate valve between plasma source and chamber was opened and the plasma ALD half-cycle was started. For the TaN process, an H_2 plasma was used; for the TiN process, we used an $\text{H}_2 - \text{N}_2$ plasma. After the plasma step, the next cycle started again with an Ar purge. Table I summarizes the details of the "baseline" conditions used throughout this work.

Table I. "Baseline" deposition conditions for remote plasma ALD of TiN and TaN films.

ALD process	TiN	TaN
ALD reactor	FlexAL	ALD-I
Substrate temperature ($^\circ\text{C}$)	350	225
Precursor:	TiCl_4	$\text{Ta}(\text{N}(\text{CH}_3)_2)_5$
Dosing time (s)	0.04	5
Temperature ($^\circ\text{C}$)	30	75
Ar pressure (mTorr)		
Plasma:		
Gas mixture		

ALD process	TiN	TaN
Pressure (mTorr)	15	7.5
Power (W)	250	100
Exposure time (s)	5	10

Thin-film analysis

In situ spectroscopic ellipsometry (SE) was used to study the thin-film growth during the deposition processes on both ALD reactors. The ellipsometer used was a J.A. Woollam, Inc. M2000U visible and near-infrared ellipsometer. A proper modeling of the dielectric function results in an accurate determination of the thickness of the deposited film.^{23, 25} Electrical sheet resistance measurements were carried out ex situ at room temperature using a Signatone four-point probe (FPP) in combination with a Keithley 2400 Source Measurement Unit, acting both as current source and voltage meter. The resistivity was obtained from the slope of the current–voltage () curve, and the film thickness was deduced from the SE measurements. The atomic compositions and areal atomic densities of the films were determined from Rutherford backscattering spectrometry and elastic recoil detection using ions. Mass densities were calculated from the areal densities using the thickness data obtained by SE. The microstructure of the films was studied using X-ray diffraction (XRD) with a Philips X'Pert MPD diffractometer equipped with a Cu source (radiation). The thickness and mass density were corroborated by X-ray reflectometry measurements performed on a Bruker D8 Advance X-ray diffractometer.

Cu and Li diffusion barrier experiments

For the Cu diffusion barrier experiments, test structures were fabricated by sputter depositing Cu films (in thickness) onto air exposed barrier films (in thickness) which were deposited on HF-last n-type silicon wafers (P-doped, resistivity of). These stacks were annealed in a vacuum oven together with control stacks that had no Cu film on top. For the FPP resistivity measurements, the samples were heated up to the anneal temperature at a ramp rate of . At the moment the anneal temperature was reached, the samples were cooled down to at a cooling rate of after which the sample was heated to the next anneal temperature. The anneal temperature was increased in steps of up to . During these thermal cycles, the sheet

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.

resistance was measured with a FPP from the top side of the test structure. In the analysis

these measurements, the sheet resistance at was considered to prevent any intrinsic influence of the temperature dependence of the Cu, TaN, TiN, and Si resistivity. The stacks for the XRD measurements were annealed using a slightly different procedure, each stack was individually heated up to the anneal temperature at a ramp rate of and kept at this temperature for , after which they were slowly cooled inside the furnace.

For the Li diffusion barrier test, cyclic voltammetry was conducted with an Autolab PGSTAT30 (Ecochemie B.V., Utrecht, The Netherlands) and galvanostatic cycling was performed using a M4300 galvanostat (Maccor, Tulsa, USA). The procedure used was identical to the one described by Baggetto et al.⁷ An n-type silicon wafer (Sb-doped, resistivity of) was used as a substrate to facilitate the electrical connection to the barrier layer. The substrate had a native oxide surface.

Results and Discussion

Remote plasma ALD of TiN and TaN films

TiN and TaN films were deposited with various plasma exposure times using the baseline conditions listed in Table I. The resulting material properties are summarized in Table II. The thickness of the TiN and TaN films is shown as a function of the number of cycles in Fig. 2. Both TiN and TaN show a linear increase in thickness with the number of cycles.

Table II. The material properties of remote plasma ALD TiN and TaN films for various plasma exposure times. In situ spectroscopic ellipsometry, Rutherford backscattering spectroscopy, and four-point probe measurements were used to determine the material properties. The typical experimental errors are shown in each column; a dash means "not measured." The deposition conditions from Table I were used unless indicated otherwise.

Plasma exposure step	Thickness (nm)	Growth per cycle (nm/cycle)	Mass density (g cm ⁻³)	Atomic composition (at %)						Electrical resistivity (μΩ cm)
				Ti	Ta	N	O	C	Cl	
TiN										
2 s H ₂ – N ₂	21.1 ± 0.2	0.035 ± 0.02	4.0 ± 0.1	49 ± 0.1	—	46	2.0	—	2.7	175 ± 15

Plasma exposure step	Thickness (nm)	Growth per cycle (nm/cycle)	Mass density (g cm^{-3})	Atomic composition (at %)						Electrical resistivity ($\mu\Omega \text{ cm}$)
				Ti	Ta	N	O	C	Cl	
5 s $\text{H}_2 - \text{N}_2$	23.2	0.039	3.9	50	—	46	2.0	—	1.8	162
10 s $\text{H}_2 - \text{N}_2$	23.5	0.039	4.0	50	—	47	2.0	—	1.3	147
20 s $\text{H}_2 - \text{N}_2$	25.2	0.042	—	—	—	—	—	—	—	145
10 s $\text{H}_2 - \text{N}_2$ a, c	31.8	0.058	—	47	—	47	3.5	—	1.9	200
5 s $\text{H}_2 - \text{N}_2$ ^b	60 ± 0.5	—	—	47	—	42	9	—	2	—
TaN										
3 s H_2	26.0 ± 0.5	0.038 ± 0.02	9.1 ± 0.5	—	42 ± 0.1	32	15	10	—	3400 ± 100
10 s H_2	31.6	0.049	10.4	—	59	29	12	< 2	—	1200
30 s H_2	28.1	0.056	12.1	—	56	25	7	12	—	380
10 s H_2 ^a	29.2	0.045	—	—	—	—	—	—	—	1550
10 s H_2 ^b	60	—	—	—	48	30	22	< 2	—	—

^aFilms used in Cu-diffusion barrier experiments. ^bFilms used in Li-diffusion barrier experiments. ^cFilm deposited using 400°C substrate temperature and a 500 W plasma with a $\text{H}_2 - \text{N}_2$ (60 – 8 sccm) gas mixture at $\sim 19 \text{ mTorr}$.

PDF

Help



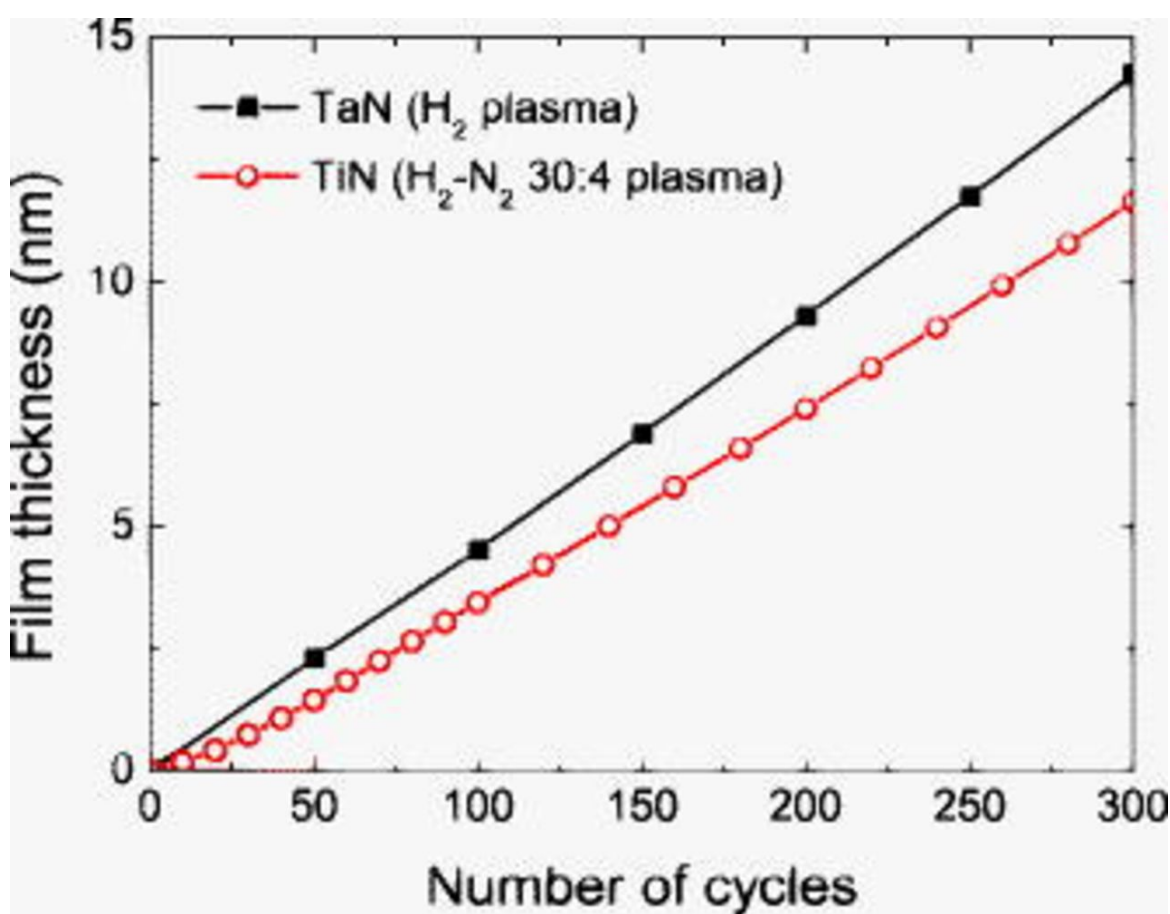


Figure 2. The thickness of the TaN and TiN films as a function of number of ALD cycles. The thicknesses have been determined by in situ spectroscopic ellipsometry.

The TiN properties showed almost no dependence on the plasma exposure time, only a slight decrease in Cl content and decrease in resistivity was observed for longer plasma exposures.

The TiN films investigated had an [N]/[Ti] ratio of 1 and all contained a relatively low level of impurities.²⁴ This is in agreement with previous work where the combination of H_2 and N_2 plasma showed excellent material properties compared to other ALD TiN processes.²⁶ Note that, for the Cu diffusion barrier experiments, slightly different deposition conditions were used (substrate temperature and a H_2 plasma with a H_2 gas mixture), which resulted in a slight increase in growth rate and resistivity.

The TaN properties depend strongly on the plasma exposure time. This can be explained by the fact that TaN can exist in many crystal phases, depending on the [Ta]/[N] ratio. Stable

crystal phases ranging from conductive to semiconductive have been reported.²⁷ The TaN

films obtained with a plasma were reasonably conductive, had a relatively low N content of 32%, and had the cubic crystal phase (see below). The N content further reduced down to 25% when the plasma exposure time was increased, which also resulted in a higher mass density and lower resistivity (as low as, Table II). mixtures and were also used as the plasma gasses, but these conditions resulted in a large increase in resistivity (e.g., for a 98:2 plasma) and even led to the semiconducting phase.²³ Because our interest lies in conductive barrier films, only films deposited by plasma were investigated in the current work.

Figures 3a and 3b show the growth per cycle and FPP resistivity of the films as a function of plasma exposure time. During the first few seconds of plasma exposure, both processes show a large increase in the growth per cycle after which saturation takes place. For TaN a so-called soft saturation behavior is observed while the saturation in growth per cycle is much clearer for the TiN case. This soft saturation can be explained by the aforementioned dependence of the material properties on the plasma exposure time (see Table II).²³ The change in material properties for TaN is also evident by the large change in resistivity with plasma exposure time (Fig. 3b). For TiN, only minor changes take place that can be attributed to a small reduction in the Cl-impurity content.

Figure 3. (a) The growth per cycle and (b) the FPP resistivity of TaN and TiN films as a function of the plasma exposure time in the ALD cycle. The lines serve as guides to the eyes.

PDF

The microstructure of the films was investigated by XRD and the measured spectra for TaN and TiN films deposited under the baseline conditions of Table I are given in Fig. 4. For both films, it is clear that the material has a cubic phase structure as can be concluded from the comparison to the powder sample data.²⁸ Both the TaN and TiN films show a strong preferential (200) growth direction compared to the powder sample. Fréty et al. found that sputtered TaN also showed a preferential (200) growth direction depending on the pressure during deposition.²² For a TaN film of deposited using plasma and precursor, Kim et al. found no preferential direction,¹⁷ while Park et al. reported an increase of the (200) peak

intensity using longer plasma exposures and tertiary imidoethers (diethylamido) tantalum



precursor.¹⁹ For sputtered TiN, a strong preferential orientation was found as well but in the (111) direction.¹⁴ In previous work, we found that for ALD TiN the preferential (200) growth direction disappears when a lower deposition temperature of was used.¹⁹ As can be seen from these literature comparisons, the microstructure depends largely on the deposition method and the process conditions used.

Figure 4. XRD spectra for (a) a thick TaN film and (b) a thick TiN film. The diffraction patterns for cubic powder samples are also given.

Cu diffusion barrier properties

The Cu diffusion barrier properties were studied in an experiment in which Cu diffusion through the barrier layer was monitored as a function of temperature in order to determine the barrier failure temperature. Evidently, a higher failure temperature indicates a higher barrier quality. Test structures were fabricated by sputter depositing Cu films onto the barrier layers as described in the experimental details. The TaN and TiN film were deposited on the Si substrates, where TaN was deposited using the baseline conditions (Table I), and the TiN film was deposited under slightly modified conditions (i.e., deposition temperature, plasma with and). These conditions result in very similar material properties as shown for the baseline conditions (Table II).

For both barrier materials, two different experiments were carried out. First, the sheet resistance of a Cu-barrier-Si stack was monitored as a function of anneal temperature. Variation of Cu sheet resistance with anneal temperature is known to provide a good measure of barrier performance.^{14, 22, 29, 30} Barrier failure leads to a significant change in resistivity due to the formation of poorly conductive ,^{14, 20, 22, 29} which will result in an increase in the sheet resistance due to the concurrent loss of Cu. As a reference, the sheet resistance of a barrier-Si stack was also measured to find possible annealing effects and to investigate the thermal stability of the barrier material itself.

Figure 5 shows the sheet resistance at of the TaN-Si, TiN-Si, Cu-TaN-Si, and the Cu-TiN-Si stacks as a function of anneal temperature. The resistance of the TaN-Si stack decreases for temperatures of . The fact that this occurs at instead of just above the deposition

PDF

Help



temperature demonstrates the thermal stability of the TaN. A similar but less pronounced annealing effect is visible for the TiN–Si stack possibly related to the higher deposition temperature of . Because of the Cu film, the Cu–TaN–Si and Cu–TiN–Si stacks show a very low sheet resistance (and , respectively), which is lost for both barriers for annealing temperatures of , when the sheet resistance suddenly increases.

Figure 5. The sheet resistance at of the TaN–Si, TiN–Si, Cu–TaN–Si, and Cu–TiN–Si stacks after heating to the anneal temperature indicated at the horizontal axis. The annealing temperature was increased in steps of up to a maximum temperature of .

To attribute the change in sheet resistance with annealing to barrier failure or another effect, a second experiment was performed; XRD spectra were measured for the stacks after annealing at different temperatures. These spectra should reveal possible formation and the concurrent loss of Cu. For completeness, it should be noted that the XRD spectra for the annealed TaN and TiN films without a Cu layer (not shown) were indistinguishable from the original (not-annealed) film. This indicates that the reduction in resistivity of the TiN and TaN in the TiN–Si and TaN–Si stacks shown in Fig. 5 is not caused by a measurable change in microstructure.

The XRD spectra for the Cu–TaN–Si stacks annealed at 200, 400, 600, 650, and are shown in Fig. 6. The most intense lines for the diffraction patterns of powder samples of cubic TaN, Cu, and are also indicated in Fig. 6. Three observations can be made when comparing the PDF XRD spectra: (i) the TaN lines are not affected by the anneal, (ii) the intensity of the Cu lines drops for the samples annealed at 650 and , and, most importantly, (iii) lines appear for the samples annealed above . These lines are best visible at values of 65 and . These observations are therefore in agreement with the result obtained by the sheet resistance measurements (i.e., between 600 and Cu starts diffusing through the TaN film and the barrier fails).

Figure 6. XRD spectra of Cu–TaN–Si stacks with of Cu and of TaN. Spectra are given for samples annealed at 200, 400, 600, 650, and . The most intense lines for the diffraction pattern of cubic TaN, Cu, and powder samples are indicated. The spectra are shifted vertically for clarity.

For sputtered TaN films ranging from thick, it has been reported that Cu diffusion starts between 650 and ,^{13, 29, 31} where the rate of diffusion is lower for films with higher N content.²⁹ Kim et al. reported a failure temperature of for a thick film deposited by ALD using a plasma.¹⁷ The same group also reported that similar to sputtered barrier films an increase in N content further increases the failure temperature.^{17, 21} However, it should also be noted that increasing the N content of the TaN film increases the resistivity, which can be undesirable in barrier applications. Our results are in qualitative agreement with those reported in literature, considering the fact that a lower failure temperature was observed for TaN films with lower N content (, Table II). Moreover, a difference in microstructure can also have a large effect on failure temperature.^{17, 20} We observed a preferential (200) growth direction while Kim et al. did not report such a preferential growth direction.¹⁷ This is a factor that likely contributes to the difference in failure temperature because a strong preferential growth can be related to a columnar microstructure, which gives rise to fast diffusion pathways.^{22, 29}

The XRD spectra for the Cu–TiN–Si stacks annealed at 200, 400, 600, and are shown in Fig. 7. The most intense lines for the diffraction patterns of powder samples of cubic TiN, Cu, and are also indicated in Fig. 7. Two conclusions can be drawn when comparing the XRD spectra: the TiN lines are not affected by the anneal and the Cu lines become more intense and narrower for higher anneal temperatures. Most importantly, no lines are observed, which points to no barrier failure up to a temperature of .

PDF

Help



Figure 7. XRD spectra of Cu–TiN–Si stacks with of Cu and of TiN. Spectra are given for samples annealed at 200, 400, 600, and . The most intense lines for the diffraction pattern of cubic TiN, Cu, and powder samples are indicated. The spectra are shifted vertically for clarity.

To further investigate the evolution of the Cu in the stack with anneal temperature for both the Cu–TaN–Si and Cu–TiN–Si stacks, the intensity of the strong Cu(111) peak () was determined and the crystallite size was obtained from the full width at half maximum of this peak using Scherrer's equation.³² Figures 8a and 8b show the intensity and the crystallite size vs anneal temperature for Cu(111) in the Cu–TaN–Si and Cu–TiN–Si stacks, respectively. The Cu peak intensity shows an increase with anneal temperature for both TaN and TiN up to , indicating Cu crystallization. The Cu crystallization is in agreement with the FPP results in Fig. 5, showing a small decrease in resistance. Similar increases in Cu(111) intensity have been reported in the literature.^{13, 14, 29, 31} Above an anneal temperature of , the Cu peak intensity from the Cu–TaN–Si stack shows a strong decrease as also expected from the peak appearance and the strong increase in sheet resistance. A completely different behavior is observed for Cu in the Cu–TiN–Si stack. The intensity increases strongly while the crystallite size also increases slightly, especially for a temperature of . This suggests a strong crystallization behavior that can be related to high bulk diffusion inside the Cu above due to its low melting point .

Figure 8. Peak intensity and crystallite size (derived using Scherrer's equation) of the Cu(111) peak in the XRD spectra for (a) Cu–TaN–Si (Fig. 6) and (b) Cu–TiN–Si (Fig. 7) stacks annealed at different temperatures.

PDF
Help

Because no peaks are formed and the Cu peak intensity is not decreasing for the Cu–TiN–Si stack, the increase in sheet resistance for temperatures of in Fig. 5 cannot be explained by the loss of Cu. Figure 9 shows scanning electron microscope (SEM) images of the surface of the Cu–TiN–Si stack: the as-deposited film (Fig. 9a) shows a smooth surface compared to the annealed Cu surface (Fig. 9b), which reveals a clear roughening of the Cu film. Annealing is

reported to cause roughening of Cu films on poorly wettable surfaces such as TiN.^{33, 34} When a larger area is observed (width, Fig. 9c), a discontinuous Cu film is visible. The discontinuous Cu film explains why the resistance increases for temperatures of .³⁵ Because of the large crystallite growth above , poorly connected islands are formed, resulting in an increase in sheet resistance. Apparently the Cu film is not thick enough to prevent this effect. Contrary to TiN, Ta-rich TaN, which is used for the Cu–TaN–Si stacks, has been reported to have excellent wettability for Cu.³⁶ For TiN, the resistance increase is therefore not caused by Cu diffusion through the barrier, suggesting excellent barrier properties. A method to improve the wettability of TiN by surface treatments will be reported in a future publication.³⁷

Figure 9. SEM images of the Cu–TiN–Si stack: (a) the smooth as-deposited Cu film and (b) the roughened Cu film after annealing at . (c) The as-deposited closed Cu film has become discontinuous after annealing, exposing areas of the underlying surface.

For stacks with of sputtered TiN, failure temperatures were reported ranging from for increasing TiN mass density .¹⁴ It is interesting to note that the density of the films in our work is lower (, Table II) while the barrier properties are still good up to . Uhm and Jeon reported a resistance increase using FPP measurements at temperatures above , peaks in XRD spectra at , and small defects using an etch pit test at for ALD TiN films deposited at using and .³⁸ Comparing these failure temperatures to our results indicate excellent barrier properties for the TiN films deposited by remote plasma ALD.

PDF

Help

Li diffusion barrier properties

In 3D integrated all-solid-state batteries, the barrier layers must prevent diffusion of Li from the active battery layers into the substrate over the entire electrochemical potential range used. A thin barrier layer is desired while maintaining the barrier properties and sufficient electrical conduction. Baggetto et al. reported the feasibility of using sputtered TaN and TiN films as planar Li diffusion barriers.⁷ To assess the prospects of using high aspect ratio structures in future 3D batteries, TaN and TiN films deposited with ALD were investigated in this work.

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



To do so, the electrochemical properties of thick planar TiN and TaN films deposited by remote plasma ALD under the baseline conditions were studied (see Table I and II). Figure 10 shows cyclic voltammograms of the films measured in a Li-containing electrolyte solution under the experimental conditions as described by Baggetto et al.⁷ The TiN film shows a very low current over the entire potential range, indicating low reactivity toward Li and demonstrating its capability as Li diffusion barrier. The reactivity of the TaN film is much higher than that of the TiN film, as indicated by the intensity of the current peaks at and . These peaks can be ascribed to tantalate structures, such as ,³⁹ which are known to be active intercalation materials below . As can be seen from the atomic composition (Table II), a significant fraction of oxygen is present in the TaN films. When the TaN film is exposed to cycles of constant-current charging and discharging, an experiment that provides information about the amount of charge involved during continuous cycling, an intercalation response into silicon is observed after a few cycles (not presented here). This response means that the actual TaN films do not prevent the penetration of Li ions into the bulk of silicon. For the TiN film, the barrier performs well under this galvanostatic cycling and it has an even lower Li intercalation capacity than a thick sputtered TiN film as shown in Fig. 11.

Figure 10. Cyclic voltammetric scans at of thick TaN and TiN films showing the reaction of the films toward Li ions.

Figure 11. Galvanostatic cycling for TiN prepared by sputtering and remote plasma ALD at a constant current of . The remote plasma ALD TiN film shows a lower capacity for Li, indicating better barrier properties.

PDF

Help

Obviously, for the TaN film, the reactivity toward Li is too high. However, because TaN can have a wide range of compositions, tuning the composition might provide adequate barrier properties for certain TaN films deposited by ALD. From the current results, it is already clear

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



that TiN deposited by remote plasma ALD is a very promising candidate for Li diffusion barrier applications. For sputtered films, TiN also showed better characteristics than TaN,⁷ while the ALD grown TiN films exhibit an even lower Li capacity.

Conclusions

Remote plasma ALD of TaN and TiN films has been investigated using the combinations of precursor with plasma and precursor with plasma, respectively. Cubic metal nitride films with a relatively low electrical resistivity (TaN: ; TiN:) can be deposited for both materials with the properties of the TaN material strongly depending on the plasma exposure time.

Furthermore, diffusion barrier tests have been carried out with respect to the anticipated application of the materials as Cu and Li diffusion barriers. TaN films show a good Cu barrier performance up to 600 ° C, as found by FPP and XRD experiments. For TiN films, no Cu diffusion was observed up to a temperature of 700 ° C. However, in this case the Cu film became discontinuous at annealing temperatures of 600 ° C due to roughening, causing a large increase in electrical resistance.

The first Li diffusion barrier experiments show that the TiN film is a very promising Li barrier, whereas the TaN barrier layers need further improvement. Consequently, both Cu and Li diffusion barrier experiments indicate better barrier properties for the TiN films, suggesting that the TiN films prepared by remote plasma ALD yields an overall better barrier performance than the TaN films prepared by remote plasma ALD. Although it is unclear for the moment whether the difference in Cu barrier performance is an intrinsic material property or due to the difference in process conditions used (such as halide precursor at high substrate temperature of 400 ° C for TiN and metallorganic precursor at lower substrate temperature of 225 ° C for TaN), future work will focus on TiN addressing its barrier properties when deposited in high aspect ratio structures required for future 3D-SiP devices.

PDF

Help

Acknowledgments

The sputter deposition of thin Cu layers and the diffusion barrier tests were carried out by Philips Research. Determination of the film composition and microstructure was carried out at the Philips Research Materials Analysis Lab. Dr. S. B. S. Heil and W. Keuning are acknowledged for their contribution to the measurements and for the insightful discussions.

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



This work was sponsored by the Materials Innovation Institute M2i under project no. MC3.06278 (the former Netherlands Institute for Metals Research), and by SenterNovem (project 'INNOVia', no. IS044041).

Eindhoven University of Technology assisted in meeting the publication costs of this article.

You may also like

JOURNAL ARTICLES

Dissolution Inhibition in Cu-CMP Using Dodecyl-Benzene-Sulfonic Acid Surfactant with Oxalic Acid and Glycine as Complexing Agents

Oxygen Reduction Reaction on Platinum/Tantalum Oxide Electrocatalysts for PEM Fuel Cells

Conduction Mechanisms of Ta/Porous SiCOH Films under Electrical Bias

High-Performance MIM Capacitors Using a High- κ TiZrO Dielectric

Temperature Dependence of the Current Conduction Mechanisms in Sm_2O_3 Thin Films

Mn^{4+} -Activated Red Photoluminescence in K_2SiF_6 Phosphor



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



[PDF](#)[Help](#)

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our [Privacy and Cookies policy](#).



PDF

Help

This site uses cookies. By continuing to use this site you agree to our use of cookies. To find out more, see our Privacy and Cookies policy.



ATTACHMENT F

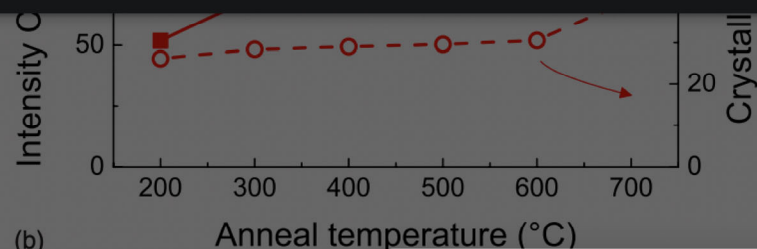


Figure 8. (Color online) Peak intensity (Scherrer's equation) of the Cu(111) peak for TaN-Si (Fig. 6) and (b) Cu-TiN-Si at various temperatures.

TaN-Si stack shows a strong decrease in the Cu_3Si peak appearance and the stack shows a completely different behavior is observed. The intensity increases strongly with temperature, suggesting a strong crystallization of the Cu film. The intensity increases slightly, especially for temperatures above 600°C, suggesting a strong crystallization of the Cu film.

Because no Cu_3Si peaks are found, the intensity is not decreasing for the Cu-TiN-Si stack for temperatures of $>600^\circ\text{C}$. Figure 9 shows SEM images of the surface of the Cu-TiN-Si stack. Figure 9(a) shows a smooth surface of the Cu surface (Fig. 9b), which reveals a smooth surface. Annealing is reported to be a poor wettability for surfaces such as TaN-Si, which is observed (30 μm width, Fig. 9c). The discontinuous Cu film explains the increase in sheet resistance. Above 600°C, poorly connected Cu film leads to an increase in sheet resistance. Appropriate thickness is thick enough to prevent this effect. The Cu-TiN-Si stack, which is used for the Cu-TaN-Si stacks, has been reported to have excellent wettability for Cu.³⁶ For TiN, the resistance increase is therefore not caused by Cu diffusion through the barrier, suggesting excellent barrier properties. A method to improve the wettability of TiN by surface treatments will be reported in a future publication.³⁷

shows cyclic voltammograms of the films measured in a Li-containing electrolyte solution under the experimental conditions as described by Baggetto et al.⁷ The TiN film shows a very low current over the entire potential range, indicating low reactivity toward Li and demonstrating its capability as Li diffusion barrier. The reactivity of the TaN film is much higher than that of the TiN film, as indicated by the intensity of the current peaks at ~ 1 and 1.5 V. These peaks can be ascribed to tantalate structures, such as Ta_2O_5 ,³⁹

intercalation materials below 1.5 V. For the TaN film, a significant intercalation response (Table II), a significant intercalation response is observed during charging and discharging, an intercalation response into the TaN film (not presented here). This intercalation response does not prevent the penetration of Li. For the TiN film, the barrier properties are excellent during cycling and it has an even lower Li capacity than a 70 nm thick sputtered TiN film.

The reactivity toward Li is too high. For the TaN film, a wide range of compositions, tunable barrier properties for TaN. From the current results, it is clear that remote plasma ALD is a very good barrier applications. For sputtered TaN, the barrier characteristics are better than TaN,⁷ while the TiN film has even lower Li capacity.

ons

TiN films has been investigated for the TaN-Si stack. The TaN-Si stack was deposited with H_2 plasma, respectively. Cubic metal TaN-Si stack has a low electrical resistivity (TaN: $\sim 10^{-4} \Omega\text{cm}$). The TaN-Si stack was deposited for both materials and the barrier properties are strongly depending on the

Furthermore, diffusion barrier tests have been carried out with respect to the anticipated application of the materials as Cu and Li diffusion barriers. TaN films show a good Cu barrier performance up to 600°C, as found by FPP and XRD experiments. For TiN films, no Cu diffusion was observed up to a temperature of 700°C. However,

Document properties

File name:	pdf
File size:	1,201 KB
Title:	-
Author:	-
Subject:	-
Keywords:	-
Created:	10/10/08, 4:09:22 AM
Modified:	12/10/22, 2:28:44 PM
Application:	XPP
PDF producer:	Acrobat Distiller 6.0.1 (Windows); modified using i...
PDF version:	1.4
Page count:	9
Page size:	Varies

Fast web view: No

Close