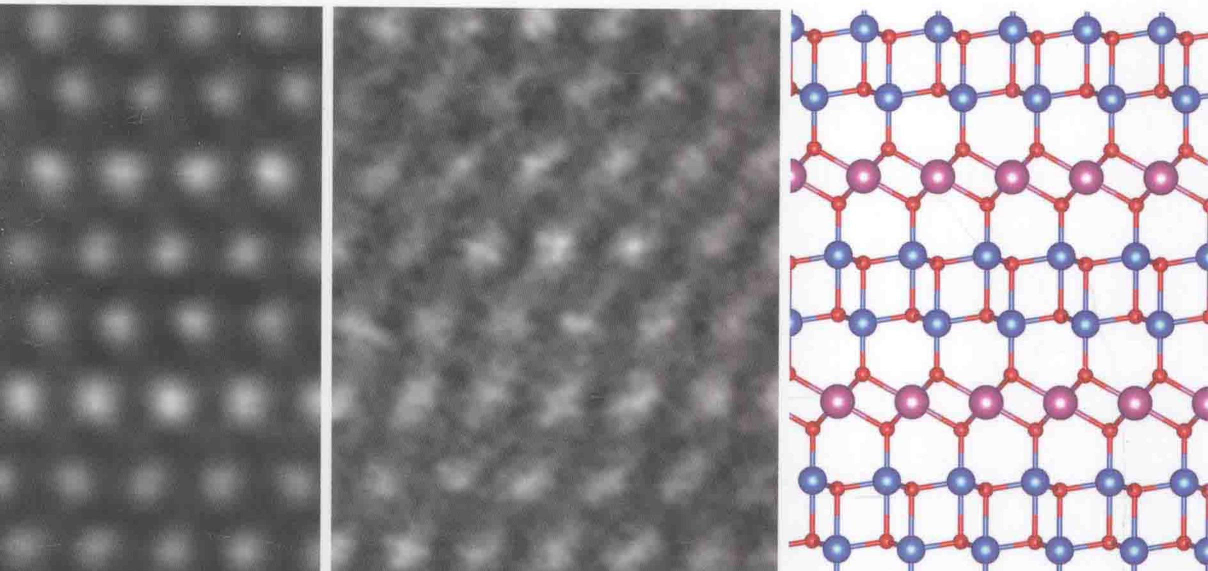
PHYSICS AND TECHNOLOGY OF
CRYSTALLINE OXIDE SEMICONDUCTOR CAAC-IGZO

FUNDAMENTALS

Edited by
Noboru Kimizuka and Shunpei Yamazaki



WILEY SID Series in Display Technology

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WILEY

This edition first published 2017

Registered Office
John Wiley & Sons, Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Names: Yamazaki, Shunpei, 1942– author. | Kimizuku, Noboru, 1940– author.
Title: Physics and technology of crystalline oxide semiconductor CAAC-IGZO. Fundamentals / Shunpei Yamazaki, Noboru Kimizuku.
Other titles: Wiley SID series in display technology.
Description: Chichester, UK ; Hoboken, NJ : John Wiley & Sons, 2016. | Series: Wiley-sid series in display technology | Includes index.
Identifiers: LCCN 2016022217 (print) | LCCN 2016033467 (ebook) | ISBN 9781119247401 (cloth) | ISBN 9781119247364 (pdf) | ISBN 9781119247371 (epub)
Subjects: LCSH: Semiconductors–Materials. | Semiconductors–Characterization. | Gallium compounds. | Zinc compounds.
Classification: LCC TK7871.85 .Y3576 2016 (print) | LCC TK7871.85 (ebook) | DDC 621.3815/2–dc23
LC record available at https://lccn.loc.gov/2016022217

A catalogue record for this book is available from the British Library.

Set in 10/12pt Times by SPi Global, Pondicherry, India
Printed and bound in Malaysia by Vivar Printing Sdn Bhd

1 2017

About the Editors

Noboru Kimizuka is director of the Kimizuka Institute for Natural Philosophy in Poland and an adviser to Semiconductor Energy Laboratory Co., Ltd. He received a Doctor of Science degree from Tokyo Institute of Technology. He joined the National Institute for Research in Inorganic Materials (NIRIM) of the Science and Technology Agency in 1967 (this later became the National Institute for Materials Science). In 1985, he synthesized crystalline IGZO for the first time in the world at NIRIM. He then devoted himself to developing homologous IGZO for about the next ten years. After leaving NIRIM, he served as a researcher and visiting professor, teaching young people at universities in the USA, UK, Mexico, Taiwan, South Korea, and Japan. He is a member of the Chemical Society of Japan, the Ceramic Society of Japan, the Physical Society of Japan, and the American Ceramic Society. He is a resident of Poland.

1967	Completed Master's Degree Program at Waseda University Faculty of Science and Engineering
1967–1994	National Institute for Research in Inorganic Materials, Science and Technology Agency 1994–1995: Guest Researcher April 1983: Group Leader April 1975: Senior Researcher April 1967: Engineering Official of General Administrative Agency of the Cabinet
1969	Awarded by Joint Committee on Powder Diffraction Standards (JCPDS)
1969–1970	Foreign Researcher, Department of Materials Science, Pennsylvania State University (USA)
1977	Ceramographic Award of the Ceramic Society of Japan
1979–1980	Foreign Researcher, Department of Chemical Engineering, University of Texas at Austin (USA)
1993–1994	Instructor, Interdisciplinary Graduate School of Science and Engineering of Tokyo Institute of Technology
1994	Foreign Researcher, Department of Chemistry, University of Aberdeen (UK)

1994 Award by the Minister of the Science and Technology Agency of Japan
1994–1996 Dispatched Long-Term Expert, Japan International Cooperation Agency (JICA)
1994–2001 Research Professor, Universidad de Sonora (Mexico)
2001–2003 Visiting Scholar, Ceramic Material Research Institute, Hanyang University (South Korea)
2003–2005 Guest Researcher, National Institute for Materials Science (NIMS)
2006 Guest Professor, Department of Chemical Engineering & Material Science, Yuan Ze University (Taiwan)
2009–2010 Guest Professor, Department of Physics, Faculty of Science, Okayama University
2013 Guest Professor, Universidad de Sonora (Mexico)

Shunpei Yamazaki received his Ph.D., ME, BE, and honorary degrees from Doshisha University, Japan, in 1971, 1967, 1965, and 2011, respectively, and is the founder and president of Semiconductor Energy Laboratory Co., Ltd. He invented a basic device structure of non-volatile memory known as "flash memory" in 1970 during his Ph.D. program. Yamazaki is a distinguished foreign member of the Royal Swedish Academy of Engineering Sciences and a founder of Kato & Yamazaki Educational Foundation. Yamazaki has published or co-published over 400 papers and conference presentations and is the inventor or co-inventor of over 6314 patents (Guinness World Record in 2011).

1967 Completed Master's Degree Program at Doshisha University Graduate School of Engineering
1970 Invented a basic device of flash memory (Japanese Patent No. 886343; Japanese Examined Patent Application Publication No. Sho50-36955)
1971 Received Ph.D. in Engineering from Doshisha University Graduate School Doctoral Program
Joined TDK Corporation (formerly TDK Electronics Co., Ltd.)
1980 Established Semiconductor Energy Laboratory Co., Ltd. and assumed position as president
1984 Awarded the Richard M. Fulrath Award by the American Ceramic Society (for research on MIS structure)
1995 Awarded the Medal with Dark Blue Ribbon from the Cabinet Office of the Japanese government (proceeds given to Japanese Red Cross Society) (awarded 6 times since 2015)
1997 Awarded the Medal with Purple Ribbon from the Cabinet Office of the Japanese government (for development of MOS LSI element technology)
2009 IVA (Royal Swedish Academy of Engineering Science) Foreign Member
2010 Awarded Okochi Memorial Technology Award from Okochi Memorial Foundation
2011 IEEE Life Fellow
Received Honorary Doctor Degree of Culture from Doshisha University
Renewed his first Guinness World Record in 2004 (man holding the most patents in the world)
2015 Granted the title of "Friend of Doshisha" by Doshisha University
2015 SID Special Recognition Award for "discovering CAAC-IGZO semiconductors, leading their practical application, and paving the way to next-generation displays by developing new information-display devices such as foldable or 8 K × 4 K displays"

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Series Editor's Foreword

The introduction of active matrix backplanes into mainstream display technologies has arguably been more significant for the development of man–machine interaction than any one of the electro-optic effects which are exploited. Universally, the large and high-quality displays we use every day rely on active matrix switching, with only the smallest and simplest devices using passive addressing.

A variety of semiconductor materials and devices have been explored for this purpose: the performance advantages of compound semiconductors (such as cadmium selenide) have been well rehearsed, and polycrystalline silicon as well as single-crystal silicon have long been exploited for high-resolution applications. However, since the 1980s, hydrogenated amorphous silicon (a-Si:H) has become established as the commodity route to high-quality liquid crystal displays and has been overwhelmingly the dominant approach to their manufacture. Now this dominance is challenged, on the one hand by the promise of reduced manufacturing costs through the use of low-temperature and solution-processed materials and on the other hand with the drive towards higher pixel counts and resolution, as well as the introduction of active matrix OLED displays, having prompted a re-examination of crystallised forms of silicon and of amorphous and crystalline oxide-based semiconductors.

The present volume is the first in a series of three books which are planned to provide a comprehensive account of one approach to oxide semiconductor technology – the *c*-axis-aligned crystal (CAAC) morphology. The CAAC approach provides TFTs with high mobility and extremely low leakage current, and moreover avoids the stability problems found in some other oxide devices. Dr. Yamazaki and his co-authors bring to this topic not only their outstanding knowledge and research background, but also a real passion for explaining the properties and applications of the materials and devices they describe.

This book takes the reader from the deposition equipment and conditions needed to obtain CAAC oxide materials, through accounts of their structure and properties, to the properties and advantages of CAAC TFTs. A full account of the structural characterisation of the materials is included, together with their interpretation, as well as descriptions of the special measurement methods needed to understand these materials and the performance of CAAC TFTs, together with a comparison with silicon devices. A brief account of the applications of CAAC oxide semiconductors concludes the volume.

Further series volumes will provide detailed accounts of the application of CAAC oxides to LSI (including imaging sensor) applications, and to displays. The value of CAAC oxide systems has already been demonstrated by the production of a number of exceptional high-resolution and high-complexity displays. As this exciting field develops, we expect that these books will provide the reader with a definitive source work and technical reference.

Ian Sage
Malvern, UK, 2016

Preface

Entering the 21st century, it seems that the growth of the electronics industry is hitting saturation level, even though it is the largest industry in the world. This is because the amount of energy used by people, which has already become enormous – as reflected in the abrupt climate change in recent years – is going to increase even more with its growth. Especially, the energy consumptions of cloud computing and electronic devices such as smartphones and supercomputers will continue to increase. Therefore, it is not an exaggeration to say that the development of new energy-saving devices has a direct influence on the continued existence of all mankind.

For this reason, we started extensive research on crystalline oxide semiconductors (OS), especially on a *c*-axis-aligned crystalline indium–gallium–zinc oxide (CAAC-IGZO) semiconductor. Due to the economic downturn in the aftermath of the Lehman Brothers' bankruptcy in the autumn of 2008, many companies withdrew from research on this subject, but I never gave up and our research in this area has continued to the present day. One of the most important characteristics of a field-effect transistor (FET) using this wide-gap semiconductor is that the off-state current is on the order of yoctoampère per centimeter (10^{-24} A/cm) (yocto is the smallest SI prefix), which is smaller than that of any other device measured so far. This characteristic effectively reduces the energy consumption, and thus we believe that it coincides with society's need to save energy.

It has been less than 10 years since I started researching and developing oxide semiconductors, but I think that proposing their effectiveness without delay is the first step toward a contribution to humanity. That is why I would like to introduce this book series, *Physics and Technology of Crystalline Oxide Semiconductor*, consisting of *Fundamentals*, *Application to LSI*, and *Application to Displays*, even though I know that it cannot be said that every detail is completely covered in the book series.

The book series contains the discovery of CAAC-IGZO by me, Shunpei Yamazaki, one of the editors and authors thereof, as well as the research results on its application obtained at Semiconductor Energy Laboratory Co., Ltd. (SEL), where I serve as president. We have decided to write the experimental facts down in as much detail as possible, and publish models whose principles have yet been verified. The reason is that I would like to give a couple of hints to readers – graduate students, on-site researchers, and developers – so that they can conduct further R&D as soon as possible. For these reasons, as well as the limited number of pages, I would like you to accept my deepest apologies for not being able to publish all of the data in these books. Even after the publication of these three books about crystalline oxide semiconductors, I would like to continue making our CAAC-IGZO technology known to the public by conducting further research on it from both engineering and academic points of view.

This book covers a wide range of topics such as an In_2O_3–Ga_2O_3–ZnO-based material, related compounds thereof, and devices (displays and LSI) using a CAAC-IGZO. Regarding this book, for those who want to know more about the IGZO crystal, please start reading from Chapter 1. If you would like to know how to make CAAC-IGZO films, please turn to Chapter 2. For all those among you who would like to know more about the physical properties of IGZO, please begin with Chapter 3. If you would like to know CAAC-IGZO's applications, please start from Chapter 4.

In the past, Bell Laboratories published a set of books called *The Bell Telephone Laboratories series* about the invention of transistors and research results thereof, which accordingly spread the current concept of transistors throughout the world. We sincerely hope that our book series will help to spread the CAAC-IGZO technology just as *The Bell Telephone Laboratories series* helped to popularize the concept of transistors. I think that CAAC-OS, especially CAAC-IGZO, still has many unexplored possibilities and thus more institutions and scientists should research it in cooperation with each other. I am expecting that the CAAC-IGZO which we discovered will flourish in the 21st century, by publishing its physical properties and principles, as well as by applying it in the display and LSI fields, especially in energy-saving devices.

So far, we have made some efforts by submitting papers and giving presentations at various conferences about crystalline oxide semiconductors and OS FETs. However, we have never heard of another case where a ceramic was used for an active element on a mass-production basis in Si LSI or displays; thus, many companies (with the exception of Sharp Corporation) will face a lot of difficulties in terms of mass production. Note that a ceramic with an amorphous structure has been proposed before, but it was not put into practical use due to reliability problems. Especially, the great depression following 2008 made many companies quit their R&D of ceramics with an amorphous structure, which was deemed to be fruitless because a FET utilizing amorphous ceramic lacks reliability. The actual reasons are that many oxygen vacancies (V_O) as well as hydrogenated oxygen vacancies generated by hydrogen trapped in V_O exist in a less-crystallized IGZO. This book also covers that point.

I, Shunpei Yamazaki, observed a TEM image of an IGZO film in front of a TEM screen to find a solution for this reliability issue. At that time, I discovered that a CAAC structure existed in the IGZO film. I thought that the problem of reliability could be solved by the use of this kind of material, and thus shifted the focus of our R&D to CAAC-IGZO. A FET using this CAAC-IGZO has a high level of reliability, which cannot be said about FETs which use amorphous IGZO. Thus, a FET with CAAC-IGZO is excellent from a repeatability point of view in that it can be measured and evaluated stably, both on the material and device level. As a result of the stable measurement and evaluation, we discovered that the off-state current is on the order of yoctoamps per centimeter (10^{-24} A/cm), as mentioned above. Additionally, since IGZO has a wide solid-solution phase, we succeeded in fabricating FETs using CAAC-IGZOs having high mobilities of 30–70 cm^2/V-s, thus exceeding 50 cm^2/V-s, by changing the composition ratio and the device structure. A mobility equaling that of an LTPS-FET means that the CAAC-IGZO might not only be able to fight evenly with an LTPS-FET, but outperform it in the industry. Furthermore, we tried to apply CAAC-IGZO FETs to LSI, something which has never been done before, and discovered that such a FET can operate with a channel length of just 20–60 nm.

Our data has been reviewed by many specialists, but it seems that to help people understand *the true value of the crystalline oxide semiconductor*, there is still a need to further explain the numerous issues concerning fundamental properties, which have not yet been fully understood. Moreover, a lot of people gave us the same advice: to help intellectuals grasp the whole picture of the technology by publishing a series of at least three books (*Fundamentals*, *Application to LSI*, and *Application to Displays*). Accordingly, I decided to publish them. Note that almost the whole content of these books is based on our experimental data. Hence, please acknowledge SEL and Advanced Film Device Inc. (AFD Inc.), a subsidiary of SEL, as the sources of these books, unless otherwise specified.

During the creation of this book, many people helped and guided us. I would like to express my sincere appreciation especially to Dr. Noboru Kimizuka, who was the first scientist in the world to have succeeded in the synthesis of IGZO. He has given us his guidance as a corporate adviser over the past several years, and kindly accepted our offer to become an editor and co-author of *Fundamentals*.

Moreover, during the research and development on which these books are based, as well as during the writing process, many young researchers at SEL also contributed. The names of all the authors involved can be found in the List of Contributors.

We would also like to extend our heartfelt thanks to Dr. Johan Bergquist, Dr. Michio Tajima, Dr. Yoshio Waseda, and Mr. Jun Koyama for helping us with the English translation of this book – by checking for errors and giving us a great deal of advice on how to improve the text.

I was blessed with support and cooperation from many outstanding individuals. I would like to add that I could not have finished these books in such a short period of time without the efforts of Dr. Ian Sage, a Wiley-SID book series editor, who suggested the publication of the books within this time, as well as Ms. Alexandra Jackson and Ms. Nithya Sechin of John Wiley & Sons, Ltd. Last but not least, I would like to express my sincere gratitude to those publishers and authors who allowed us to use their figures as references in these books.

Shunpei Yamazaki
President of Semiconductor Energy Laboratory Co., Ltd.

Acknowledgments

First of all, we would like to thank **Dr. Johan Bergquist**, **Dr. Michio Tajima**, **Dr. Yoshio Waseda**, and **Mr. Jun Koyama**, who encouraged us and gave us valuable advice on writing manuscripts.

Furthermore, we would also like to thank many people in a variety of fields for providing data, cooperation in manuscript writing and English translation, and all other aspects of this book.

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Ms. Mayumi Adachi
Mr. Shunsuke Adachi
Mr. Kengo Akimoto
Ms. Yukari Amano
Mr. Tobias Breitling
Ms. Nana Fujii
Mr. Shuji Fukai
Mr. Takafumi Fukumoto
Mr. Kazuma Furutani
Mr. Hiromichi Godo
Ms. Ai Hattori
Mr. Masahiko Hayakawa
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Mr. Takashi Igarashi
Ms. Yasuko Iharakumi
Mr. Takayuki Inoue
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Mr. Yuto Yakubo
Mr. Ryo Yamauchi
Ms. Chiaki Yamura
and many others…

Noboru Kimizuka
Shunpei Yamazaki

Introduction

Physics and Technology of Crystalline Oxide Semiconductor CAAC-IGZO is composed of three books: *Fundamentals*, *Application to LSI*, and *Application to Displays*. Their association is shown in Figure 1.

This book, *Fundamentals*, presents characteristics of materials for an oxide semiconductor and its film-deposition mechanism. Specifically, this book covers results of atomic-level crystal structure analysis in nanometer order using high-resolution transmission electron microscopy (TEM) images, and proposes the deposition mechanism of *c*-axis-aligned crystalline indium–gallium–zinc oxide (CAAC-IGZO). Moreover, besides the fundamental properties of CAAC-IGZO, the electrical characteristics of CAAC-IGZO field-effect transistors (FETs) and a comparison of CAAC-IGZO FETs and silicon (Si) FETs are shown.

In *Physics and Technology of Crystalline Oxide Semiconductor CAAC-IGZO*, *Fundamentals* is positioned as the trunk, branching into *Application to LSI* and *Application to Displays*.

Application to LSI is expressed by one thick branch extending toward the miniaturization and integration (hybrid process) of LSI devices. It describes the process technologies of CAAC-IGZO FETs: a microfabrication process, a combination with Si process, and a combination process with other components such as wirings, insulating films, and capacitors. As fruits of these technologies, memories, CPUs, image sensors, and integrated circuits such as field-programmable gate arrays (FPGAs) are introduced.

Application to Displays is another thick branch extending toward high productivity and large-sized display devices. It describes the process technologies of CAAC-IGZO transistors: manufacturing process flows for a variety of types of transistor, a large-sized substrate, high productivity, low cost, and a combination with other components such as wirings, insulating films, and capacitors. The book covers, for application to organic light-emitting diode (OLED) displays and liquid crystal displays (LCDs) using CAAC-IGZO thin-film transistors (TFTs), TFT characteristics, driver circuits for display devices, high-resolution technology, low-power-consumption technology, transfer technology, and so on. As fruits of these technologies, a variety of prototyped displays (e.g., OLED displays, LCDs, and flexible displays) are introduced. In particular, the off-state current characteristic, which is the most outstanding feature, is explained in detail.

Figure 1 Framework of *Physics and Technology of Crystalline Oxide Semiconductor CAAC-IGZO*

The three books are closely associated with each other. Besides *Fundamentals*, *Application to LSI* and *Application to Displays* are of value to readers who might be interested in the basic theories and fabrication process of CAAC-IGZO devices. Data and references in these two books will also be useful to readers. The editors hope that this book series will be a foundation for the further development of CAAC-IGZO technology.

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