PHYSICS AND TECHNOLOGY OF CRYSTALLINE OXIDE SEMICONDUCTOR CAAC-IGZO
PHYSICS AND TECHNOLOGY OF CRYSTALLINE OXIDE SEMICONDUCTOR CAAC-IGZO FUNDAMENTALS

Edited by

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Contents

About the Editors ix
List of Contributors xi
Series Editor’s Foreword xii
Preface xiv
Acknowledgments xvii
Introduction xviii

1 Layered Compounds in the In$_2$O$_3$–Ga$_2$O$_3$–ZnO System and Related Compounds in the Ternary System 1

1.1 Introduction 1

1.2 Syntheses and Phase Equilibrium Diagrams 3

1.2.1 Phase Equilibrium Diagrams in the System R$_2$O$_3$–Fe$_2$O$_3$–FeO (R = Y and Yb) 4

1.2.2 Phase Equilibrium Diagram for the System In$_2$O$_3$–A$_2$O$_3$–BO (A = Ga and Fe; B = Zn, Mg, Cu, and Co) 6

1.2.3 Phase Equilibrium Diagram of the System In$_2$O$_3$–A$_2$O$_3$–ZnO (A = Fe and Al) 12

1.2.4 Other Layered-Structure Compounds 16

1.3 Crystal Structures 16

1.3.1 Crystal Structures of InGaO$_3$(ZnO)$_m$ (m = 1, 2, 3, and 4) 17

1.3.2 Lattice Constants of InAO$_3$(ZnO)$_m$ (A = In, Fe, Ga, and Al) 30

1.3.3 Structural Characteristics of RAO$_3$(BO)$_m$ Crystals 35

1.4 Latest Topics in Crystalline IGZO 37

1.4.1 Interest in Non-conventional Compounds, InGaO$_3$(ZnO)$_m$ (m: non-integral number) 37

1.4.2 Crystal Structures and Local Structures 38

1.4.3 Atomic Distribution in Crystalline IGZO(1:1:1.5) 41

1.4.4 Influence of Composition of Crystalline IGZO 41
Appendix 2.A  Discovery of CAAC-IGZO  135
  2.B.1  Diffraction Method  137
  2.B.2  Electron Diffraction  138
Appendix 2.C  Electron Diffraction Simulation of IGZO  142
Appendix 2.D  Quantitative Evaluation of Alignment of IGZO Using NBED Method  143
Appendix 2.E  Crystallinity of IGZO Thin Film Deposited by Pulsed Laser Deposition  147
  2.E.1  Introduction  147
  2.E.2  Crystallinity of IGZO Thin Film Deposited by Pulsed Laser Deposition  148
References  150

3  Fundamental Properties of IGZO  153
  3.1  Introduction  153
  3.2  Band Structure  155
    3.2.1  Introduction  155
    3.2.2  Optical Characteristics and Bandgap  155
    3.2.3  Band Structure and Effective Mass  158
    3.2.4  Summary  161
  3.3  Defect Levels in IGZO Bandgaps  161
    3.3.1  Introduction  161
    3.3.2  Evaluation of Oxygen Vacancy and Defect Levels in IGZO Thin Films  162
    3.3.3  Low-Temperature Photoluminescence  163
    3.3.4  Constant Photocurrent Method  163
    3.3.5  Deep Defect Level by Calculation  167
    3.3.6  Oxygen Vacancy and Crystallinity of IGZO  170
    3.3.7  Observations of Oxygen in IGZO  174
    3.3.8  Summary  177
  3.4  Origin of Main Donor  179
    3.4.1  Introduction  179
    3.4.2  Relationship between Hydrogen Concentration and Conductivity  179
    3.4.3  Quantitative Relationship between Carrier and Hydrogen Concentrations  182
    3.4.4  Stable Structure for Coexistence of Oxygen Vacancy and Hydrogen  183
    3.4.5  Energy Level of Donor States  184
    3.4.6  Thermal Stability of Hydrogen Substituting Oxygen  185
    3.4.7  Summary  189
  3.5  Electrical Conduction Mechanisms  190
    3.5.1  Introduction  190
    3.5.2  Dominant Scattering Center in Crystalline IGZO  191
    3.5.3  Theoretical Model of Electron Mobility for In-Rich IGZO  194
    3.5.4  Conclusion and Some Ideas for Conduction Mechanisms in IGZO  198
  3.6  Summary  199
Appendix 3.A  X-Ray Reflectivity and Constant Photocurrent Method  200
   3.A.1  X-Ray Reflectivity  200
   3.A.2  Constant Photocurrent Method  202
Appendix 3.B  First-Principles Calculation Methods  205
   3.B.1  Search for Stable Distribution of Ga and Zn Atoms in InGaZnO₄  206
   3.B.2  Formation of Amorphous IGZO Model  209
   3.B.3  Defect Valuation by Calculation  211
References  214

4  CAAC-IGZO Field-Effect Transistor  216
4.1  Physics of MOSFETs  216
   4.1.1  Classification of MOSFETs  217
   4.1.2  Operating Mechanism of CAAC-IGZO FET  219
   4.1.3  FET Characteristics and Performance Indexes  229
4.2  Electrical Characteristics of CAAC-IGZO FET  232
   4.2.1  Current-Voltage Characteristics of CAAC-IGZO FET  232
   4.2.2  Normally-Off Threshold Voltage of CAAC-IGZO FET  235
   4.2.3  Extremely Low Off-State Current of CAAC-IGZO FET  237
   4.2.4  Frequency Characteristics of CAAC-IGZO FET  254
4.3  Comparison between CAAC-IGZO and Si FETs  258
   4.3.1  Off-State Current  259
   4.3.2  Saturation Characteristics  260
   4.3.3  Short-Channel Effects  263
4.4  Advantages of CAAC-IGZO as FET Material  266
   4.4.1  Effects of CAAC Morphology on IGZO Thin-Film and FET Characteristics  266
   4.4.2  Application to Large-Sized Devices  272
   4.4.3  Multi-layered CAAC-IGZO  274
   4.4.4  Impurity Blocking Effects of CAAC-IGZO  280
4.5  Summary  281
References  282

5  Device Application Using CAAC-IGZO  285
5.1  Introduction  285
5.2  CAAC-IGZO FETs  286
   5.2.1  Bottom-Gate Top-Contact Structure  287
   5.2.2  Top-Gate Top-Contact Structure  292
   5.2.3  Top-Gate Self-aligned Structure  293
   5.2.4  Summary  297
5.3  Application to LSI  298
5.4  Application to Displays  304
5.5  Market Prospects  309
References  309

Appendix: Unit Prefix  311

Index  312
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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 yoctoamperes 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$_2$O$_3$–Ga$_2$O$_3$–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.
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Noboru Kimizuka
Shunpei Yamazaki
Introduction

Physics and Technology of Crystalline OxideSemiconductor 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.
Layered Compounds in the \( \text{In}_2\text{O}_3-\text{Ga}_2\text{O}_3-\text{ZnO} \) System and Related Compounds in the Ternary System

1.1 Introduction

Indium–gallium–zinc oxide (IGZO) has gained traction as a novel semiconductor material in electronics. IGZO thin-film transistors are currently employed in the backplanes of mass-produced flat-panel displays, and their potential in various devices has been discussed in recent studies. The features and physical properties of IGZO differ from those of silicon, which is widely used in electronic devices. For instance, IGZO is a multi-component oxide with three cations. Furthermore, the distinctive layered structure of IGZO has led to the discovery of a new crystal morphology, \( c \)-axis-aligned crystalline IGZO (CAAC-IGZO), which will be detailed in the following chapters. The present chapter mainly describes the phase equilibrium diagrams of multi-component oxides and crystal structures of \( \text{InGaO}_3(\text{ZnO})_m \) \( (m>0) \) with layered structures.

The properties of IGZO vary with the composition ratio of the metal elements. The bandgaps of \( \text{In}_2\text{O}_3, \text{ZnO}, \) and \( \text{Ga}_2\text{O}_3 \) (with different chemical compositions) are 2.6–2.9 [1, 2], 3.4 [3], and 4.8 eV [4], respectively. IGZO exhibits semiconductor properties in a relatively wide range of the phase equilibrium diagram. In the \( \text{ZnO}–\text{InGaZnO}_4 \) system, because \( \text{ZnO} \) and \( \text{InGaO}_3(\text{ZnO}) \) \( (m=1) \) show semiconductor properties, we speculate that a series of \( \text{InGaO}_3(\text{ZnO})_m \) will also behave as semiconductors. The \( \text{InGaO}_3(\text{ZnO})_m \) series has a layered structure in which \( \text{O}^{2-} \) is two-dimensional close-packed but may not be in contact with each other. This structure is closely related to the crystal morphology of CAAC-IGZO films, which will be described in the next chapter.
From the 1950s through the 1960s, the National Bureau of Standards [NBS, currently the National Institute of Standards and Technology (NIST)] in the United States comprehensively investigated the phase relationships of binary oxide systems such as $R_2O_3-R'_2O_3$, $R_2O_3-A_2O_3$, and $R_2O_3-TiO_2$ at temperatures up to 1800°C under atmospheric pressure. Here, $R$ and $R'$ denote lanthanides, Y, or Sc; $A$ denotes Fe, Ga, Cr, or Al. Consequently, the NBS reported the thermochemical stability and crystal structures of the cationic elements in $RAO_3$ (perovskite), $R_2A_2O_12$ (garnet), magnetoplumbite, and $R_2Ti_2O_7$ (pyrochlore) [5–7]. Independently of the NBS research, Kimizuka and coworkers [8–17] added oxides of divalent cations, $BO$, to the binary system and investigated the resulting ternary system. This investigation, performed in the 1970s, is historically important as an extension of the NBS studies to a ternary system. In their systematic search for materials, Kimizuka and colleagues experimentally determined the phase equilibrium diagrams of the $R_2O_3-A_2O_3-BO$ system at high temperatures and found a large number of $(RAO_3)_nBO$ and $RAO_3(BO)_m$. Here, $R$ is a lanthanide, Y, In, or Sc; $A$ is a trivalent cation and $B$ is a divalent cation; $m$ and $n$ are natural numbers with no identified upper limits. Subsequently, some $RAO_3(BO)_m$-type and $(RAO_3)_nBO$-type single crystals were grown, and their structures determined using single-crystal X-ray diffraction analysis. In addition, sintered powder bodies of these compounds were analyzed by powder X-ray diffraction and by electron beam diffraction. Consequently, the crystal structure of the homologous compounds $RAO_3(BO)_m$ was revealed: the $R$ cation is located within the octahedral coordination of the $O^{2-}$ anions, and the $A$ and $B$ cations are located within the trigonal-bipyramidal and tetrahedral coordination of the $O^{2-}$ anions. All cations and anions in these oxides lie on the triangular lattice, and the $O^{2-}$ anions stack perpendicular to the $c$-axis of the hexagonal crystal system [18–23]. The basic crystal structure was determined by analyzing $YbFe_2O_4$, an $RAO_3(BO)_m$ member with $m = 1$ [18]. The crystal structures of $AB_2X_4$-type compounds, classified by their coordination numbers, are listed in Table 1.1 [8, 24]. In the $YbFe_2O_4$-type crystal structure, $R^{3+}$ occupies the sites of 6-fold oxygen octahedral coordination, and the $A^{3+}$ and $B^{2+}$ cations locate in the 5-fold oxygen trigonal-bipyramidal coordination. The $InGaO_3(ZnO)_m$ group $InGaO_3(ZnO)$ is isostructural with $YbFe_2O_4$. Before the discovery of $YbFe_2O_4$, no $AB_2X_4$-type compounds with 5- and 6-fold coordination were known. Compounds with layered structures related to $RAO_3(BO)_m$, including aluminum carbonitrides [25, 26] and sulfides (containing indium, gallium, and zinc), have also been reported [27].

| CN of $A$ | CN of $B$ | $4$ | $5$ | $6$ | $8$ | $9$ and/or $10$
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<td>6</td>
<td>$YbFe_2O_4$</td>
<td>Sr$_2$PbO$_4$, Ca$_2$IrO$_4$, etc.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>CaFe$_2$O$_4$, CaTi$_2$O$_4$</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Table 1.1* Classification of crystal structures with the general formula $AB_2X_4$, based on the coordination number (CN) of their cations. *Source:* Reprinted from [8], Copyright (1985), with permission from Elsevier.
As noted above, the $R_2O_3$–$A_2O_3$–$BO$ system includes $RAO_3(BO)_m$ compounds with layered structures. In particular, layered $InGaO_3(ZnO)_m$ can be synthesized over a wide compositional range, and each $InGaO_3(ZnO)_m$ has substitutional solid solutions in the range $In_{1+x},Ga_{1-x}O_3(ZnO)_m$ ($-1 < x < 1$). Although structural uniformity is difficult to achieve in a multi-component system, such wide-ranging composition and solid solution suppresses the structural variation among the various chemical compositions. Therefore, the fundamental properties of layered crystals in the $In_2O_3$–$Ga_2O_3$–$ZnO$ system, which are not expected to vary significantly, are suitable for the mass production of semiconductor devices. Kimizuka’s elucidation of the phase equilibrium in $In_2O_3$–$Ga_2O_3$–$ZnO$ has contributed significantly to the subsequent technology and mass production of CAAC-IGZO devices.

As a prelude to the succeeding chapters, this chapter introduces the crystal structures and phase equilibrium diagrams at high temperatures in the $R_2O_3$–$A_2O_3$–$BO$ system, including the layered oxides mentioned above. Section 1.2 describes the phase equilibrium diagrams of ternary systems, including $InGaO_3(ZnO)_m$, and shows that their characteristics are not limited to the $In_2O_3$–$Ga_2O_3$–$ZnO$ system. Section 1.3 presents the crystal structure of $InGaO_3(ZnO)_m$ and its layer-stacking sequences, obtained in a crystal structure analysis of powdered and single-crystal specimens. Section 1.4 presents transmission electron microscopy (TEM) images of $InGaO_3(ZnO)_m$ (where $m$ is non-integer) with a long-period disordered stacking sequence along an axis perpendicular to the layer. The methods used to acquire the scanning TEM (STEM) images [annular bright field (ABF) and high-angle annular dark field (HAADF)] are outlined in Appendix 1.A.

## 1.2 Syntheses and Phase Equilibrium Diagrams

Here we describe what led to the discovery of $InGaZnO_4$. The first important study was on a phase equilibrium diagram of the $Y_2O_3$–$Fe_2O_3$–$FeO$ system at high temperatures [19, 28]. This system includes YFe$_2$O$_4$, a mixed-valence compound containing Fe$^{2+}$ and Fe$^{3+}$ which is isomorphous with $InGaZnO_4$. Subsequently, the phase equilibrium diagram of the $R_2O_3$–$Fe_2O_3$–$FeO$ system ($R = Ho, Er, Tm, Yb, and Lu$) was determined [29–32], and a new phase ($RFeO_3)_nFeO$ ($n > 0$) with members ($RFeO_3$) FeO, ($RFeO_3)_2$ FeO, … was found. $RFeO_3$ (FeO) and ($RFeO_3)_2$ (FeO) are isostructural with $InGaO_3(ZnO)$ and ($InGaO_3)_2ZnO$, respectively.

When determining the phase relationships of the above-mentioned systems comprising FeO, the oxygen partial pressure $P(O_2)$ must be controlled. The phase equilibrium diagrams of these systems were determined in situ using thermogravimetric analysis, controlling the $P(O_2)$ in the gas phase. Among these systems, $Y_2O_3$–$Fe_2O_3$–$FeO$ and $Yb_2O_3$–$Fe_2O_3$–$FeO$ were particularly selected as case studies in Subsection 1.2.1.

The phase equilibrium diagram of the ternary system $R_2O_3$–$A_2O_3$–$BO$ ($R$= a lanthanide element, In, or Sc; $A$ = In, Fe, Ga, or Al; $B$ = Mg, Mn, Co, Cu, or Zn) was determined from solid-phase reactions of $R_2O_3$, $A_2O_3$, and $BO$ powders [8, 11]. These compounds were synthesized with the classical quenching method, in which the starting materials were sealed in platinum tubes and the mixtures rapidly cooled in water after heating for a predetermined time. The diagrams were constructed from the crystal structures of the synthesized powders, as identified by powder X-ray diffraction and electron beam diffraction methods. For example, the following compounds were discovered: $In_2O_3(ZnO)_m$ [23, 33–37], $InAlO_3(ZnO)_m$ [16], $InFeO_3(ZnO)_m$ [10, 14, 21], ($InFeO_3)_n(CuO)_m$ [9], ($InGaO_3)_n(CuO)_m$ [9], $InFeO_3(MnO)_m$ [38], and
InGaO$_3$(MnO)$_n$ [12], all of which are isostructural with InGaO$_3$(ZnO)$_m$ [8, 11, 15, 23, 39]. Among these, the In$_2$O$_3$–Ga$_2$O$_3$–BO system ($B = \text{Zn, Mg, Cu, and Co}$) is discussed in Subsection 1.2.2.

As mentioned above, a series of phases is generally expressed by a composition formula with a certain variable (e.g., a natural number $n$). These phases are called “homologous$^1$ phases.” For example, the series of vanadium oxide compounds VO$_2$, V$_2$O$_3$, V$_3$O$_5$, ... is defined by the general formula $V_n$O$_{2n-1}$. Such phases are called Magnéli phases; meanwhile, phases with the general formula $V_n$O$_{2n+1}$ are called Wadsley phases. Although Magnéli and Wadsley phases are given by different formulae, in the context of this book, these phases belong to the homologous phase. As described in Section 1.1, the compounds InGaO$_3$(ZnO), InGaO$_3$(ZnO)$_2$, InGaO$_3$(ZnO)$_3$, ... are generally referred to as homologous-phase InGaO$_3$(ZnO)$_n$; compounds belonging to homologous phases are termed “homologous compounds,” and homologous compounds with the composition formula InGaO$_3$(ZnO) are termed “homologous InGaO$_3$(ZnO).”

1.2.1 Phase Equilibrium Diagrams in the System $R_2$O$_3$–Fe$_2$O$_3$–FeO ($R = \text{Y and Yb}$)

(RFeO$_3$) FeO ($R = \text{Y and Yb}$) and (RFeO$_3$)$_2$ FeO are isostructural with (InGaO$_3$)ZnO and (InGaO$_3$)$_2$ZnO, respectively. This subsection describes the Y$_2$O$_3$–Fe$_2$O$_3$–Fe and Yb$_2$O$_3$–Fe$_2$O$_3$–Fe systems, from which the homologous (RFeO$_3$)$_n$(BO) were synthesized. The phase equilibrium diagrams of these systems were determined in situ by thermogravimetric analysis under controlled oxygen partial pressure $P$(O$_2$). Thermogravimetric analysis directly measures the weight change of a sample heated at a constant rate using a thermobalance. The total pressure is 1 atm, and the oxygen partial pressure is controlled by the mixing ratio of the CO$_2$ and H$_2$ gas. In analyzing the above systems, the temperature was set to 1200°C, and the oxygen partial pressure (measured using a stabilized zirconia electrolyte cell) was increased from 1.0 to $1.58 \times 10^{-16}$ atm.

1.2.1.1 Y$_2$O$_3$–Fe$_2$O$_3$–FeO System at 1200°C

As mentioned above, the phase equilibrium diagram of the Y$_2$O$_3$–Fe$_2$O$_3$–Fe system was determined at 1200°C [19, 28]; we describe the subsystem Y$_2$O$_3$–Fe$_2$O$_3$–FeO. In this subsystem, Y$_2$O$_3$, Fe$_2$O$_3$ (hematite) and FeO (wüstite) have bixbyite, corundum, and rock salt structures, respectively. The binary Y$_2$O$_3$–Fe$_2$O$_3$ system includes YFeO$_3$ (distorted perovskite) and Y$_3$Fe$_5$O$_{12}$ (yttrium–iron garnet). The binary Fe$_2$O$_3$–FeO system has Fe$_3$O$_4$ (magnetite) with Fe$^{2+}$ and Fe$^{3+}$. YFe$_2$O$_4$, a new phase composed of Y$_2$O$_3$–Fe$_2$O$_3$–FeO, lies between YFeO$_3$

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$^1$The term “homologous” has various meanings in different fields. For example, in biology, “homologous” means “corresponding in structure and in origin,” as for example the wing of a bird and the foreleg of a horse [A: Random House Dictionary]. In organic chemistry, “homologous” refers to a series of organic compounds “having similar characteristics and structure but differing by a number of CH$_2$ groups” [B: Collins English Dictionary]. In crystal chemistry, the term is used for a series of compounds expressed by a general formula. For example, IGZO has a series of compounds group, e.g., In$_2$Ga$_2$Zn$_2$O$_7$, InGaZn$_2$O$_5$, InGaZn$_3$O$_6$, and so on. These compounds are called a “homologous” series.
and FeO (shown in Figure 1.1) [28]. The YFe$_2$O$_4$ phase is isostructural with InGaO$_3$(ZnO), as described later, and constitutes a mixed-valence compound with a layered structure of Fe$^{2+}$ and Fe$^{3+}$. YFe$_2$O$_4$ was grown under controlled oxygen partial pressure by the floating zone method, and its crystal structure was determined by X-ray diffraction [19].

Figure 1.1 (a) Phase equilibrium diagram of the Y$_2$O$_3$–Fe$_2$O$_3$–Fe system at 1200°C and (b) detailed phase equilibrium diagram near FeO$_{1.5}$. ●, Single phase. In (a), the numbers signify the values of the $-\log P(O_2)$ fields equilibrated with the three solid phases. Small letters (a to l) in the diagram represent a chemical composition of a single phase as in the right of this figure. In (b), capital letters (A to M, W, and Y) in the diagram represent a phase of a chemical composition: letters A to L correspond to the small letters a to l in (a); letters M, W, and Y are as shown in the right of this figure. M is magnetite solid solution, W is partial solid solution of wüstite, and Y is solid solution or partial solid solution of YFe$_2$O$_4$. Source: Adapted from [28]
This YFe$_2$O$_4$ phase is stable at oxygen partial pressures $P$(O$_2$) from $7.41 \times 10^{-11}$ to $1.14 \times 10^{-12}$ atm, and its chemical composition varies from YFe$_2$O$_{3.905}$ to YFe$_2$O$_{4.000}$. Above this $P$(O$_2$) range, it decomposes into Y$_2$O$_3$ and metallic iron ($\gamma$-iron); below this range, it dissociates into YFeO$_3$ and wüstite (FeO). This dissociation is also observed at temperatures between 900 and 1100°C at a pressure of 4.9 GPa. A melt phase emerges at 1400°C. Under atmospheric pressure at 800°C, the YFe$_2$O$_4$ phase dissociates into an E phase (with a chemical composition of Fe$_{2.957}$O$_4$) and wüstite (FeO).

1.2.1.2 Yb$_2$O$_3$–Fe$_2$O$_3$–FeO System at 1200°C

Subsequent to the Y$_2$O$_3$–Fe$_2$O$_3$–Fe system, the next phase equilibrium diagram was constructed for the Yb$_2$O$_3$–Fe$_2$O$_3$–Fe system at 1200°C [29]; we describe the subsystem Yb$_2$O$_3$–Fe$_2$O$_3$–FeO. Homologous (YbFeO$_{3-n}$)$_n$FeO ($n = 1, 2, 3,$ and 4) were found as a new phase of this ternary system. Yb$_2$O$_3$ is a sesquioxide isostructural with the mineral bixbyite, similar to the above-mentioned Y$_2$O$_3$. However, the ionic radius of Yb$^{3+}$ is smaller than that of Y$^{3+}$ [40]. As with the Y$_2$O$_3$–Fe$_2$O$_3$–Fe system, the thermal equilibrium state of this system was analyzed at 1200°C under controlled partial oxygen pressure. In the YbFeO$_3$–FeO system, YbFe$_2$O$_4$ and Yb$_2$Fe$_3$O$_7$ are stable at oxygen partial pressures $P$(O$_2$) ranging from $1.66 \times 10^{-12}$ to $5.01 \times 10^{-9}$ and $2.00 \times 10^{-10}$ to $5.01 \times 10^{-9}$ atm, respectively. Single crystals of (YbFeO$_3$) FeO and (YbFeO$_3$)$_2$FeO were grown, and their crystal structures were revealed [41]. Like the compounds in the Y$_2$O$_3$–Fe$_2$O$_3$–FeO system, the YbFe$_2$O$_4$ [18, 29] and Yb$_2$Fe$_3$O$_7$ [29, 42] in the Yb$_2$O$_3$–Fe$_2$O$_3$–FeO system are mixed-valence phases of Fe$^{2+}$ and Fe$^{3+}$. These phases are isostructural with InGaO$_3$(ZnO) and (InGaO$_3$)$_2$ZnO, respectively, as mentioned later. Figure 1.2 shows the phase equilibrium diagram of the Yb$_2$O$_3$–Fe$_2$O$_3$–FeO system at 1200°C. Note that Yb$_3$Fe$_2$O$_{10}$ and Yb$_4$Fe$_5$O$_{13}$ are generated as the heating temperature increases [43, 44].

1.2.2 Phase Equilibrium Diagram for the System In$_2$O$_3$–A$_2$O$_3$–BO

(A = Ga and Fe; B = Zn, Mg, Cu, and Co)

In the phase equilibrium diagrams of the system R$_2$O$_3$–Fe$_2$O$_3$–FeO (R = Y and Yb), new phases were found; namely, YFe$_2$O$_4$ and (YbFeO$_3$)$_n$(FeO) ($n = 1, 2, 3,$ and 4). Subsequently, the lanthanide element was replaced with an element of smaller ionic radius (indium), and the phase equilibrium diagram of the resulting system In$_2$O$_3$–A$_2$O$_3$–BO (where A is a trivalent cation and B is a divalent cation) was comprehensively investigated.

This subsection focuses on the relationship between the component BO (B = Zn, Mg, Cu, and Co) and the phase equilibrium diagram of the system In$_2$O$_3$–Ga$_2$O$_3$–BO. In these systems, each oxide has the following features: indium has a smaller ionic radius than a lanthanide; In$_2$O$_3$, like Y$_2$O$_3$ and Yb$_2$O$_3$, is isostructural with the mineral bixbyite. The indium cation in the oxide is trivalent with 4-, 5-, 6-, and 8-fold coordination [40]. In contrast, 4- and 5-fold coordination is unknown in rare-earth elements. The gallium oxide is isostructural with $\beta$-Ga$_2$O$_3$. The trivalent gallium cation has coordination numbers of four, five, and six. Empirically, trivalent gallium cations are known to favor four-coordinate cations more than trivalent iron cations. The divalent cations ($B^{2+}$) of Zn$^{2+}$, Co$^{2+}$, and Cu$^{2+}$ are more inclined to be 4-fold coordinated.
than Fe$^{2+}$. The 4-fold coordination geometry of Co$^{2+}$ and Cu$^{2+}$ differs from that of Zn$^{2+}$, resulting in the difference in their crystallographic behavior.

In Subsections 1.2.2.1–1.2.2.4 we explain the phase equilibrium diagrams of two In$_2$O$_3$–Ga$_2$O$_3$–BO systems. In the first instance, $B = \text{Zn}$; in the second instance, $B = \text{Mg, Cu, and Co}$. 

Figure 1.2 (a) Phase diagram of the system Yb$_2$O$_3$–Fe$_2$O$_3$–Fe at 1200°C and (b) detailed phase equilibrium diagram near FeO$_{1.5}$. ●. Experimental results. In (a), the numbers signify the values of the $-\log P(O_2)$ fields equilibrated with the three solid phases. Small letters (a to n, p, q, and y) in the diagram represent a chemical composition as in the right of this figure. In (b), capital letters in the diagram represent a phase corresponding to a chemical composition as in the right of this figure. These letters correspond to the small letters in (a). Solid solution of YbFe$_2$O$_4$ and Yb$_2$Fe$_3$O$_7$ exists in the range from l to n, and from j to k. YbFe$_2$O$_4$ and Yb$_2$Fe$_3$O$_7$ belong to homologous (YbFeO$_3$)$_n$(FeO). Source: Adapted from [29]
1.2.2.1 In$_2$O$_3$–Ga$_2$O$_3$–ZnO System at 1350°C

Under atmospheric pressure, the In$_2$O$_3$, Ga$_2$O$_3$, and ZnO in the In$_2$O$_3$–Ga$_2$O$_3$–ZnO system exhibit a bixbyite-type structure, a β-Ga$_2$O$_3$-type structure, and a wurtzite-type structure, respectively. At high temperature, Ga$_2$O$_3$ is a mineral corundum, as is Fe$_2$O$_3$. The In$_2$O$_3$–ZnO system contains hexagonal In$_2$O$_3$\((\text{ZnO})_m\), whereas the Ga$_2$O$_3$–ZnO system contains orthorhombic Ga$_2$O$_3$\((\text{ZnO})_m\). Likewise, the In$_2$O$_3$–Ga$_2$O$_3$–ZnO system contains (InGaO$_3$)$_2$ZnO and InGaO$_3$\((\text{ZnO})_m\). Figure 1.3 shows the phase diagram of the In$_2$O$_3$–Ga$_2$O$_3$–ZnO system. The regions (1)–(5) in this figure are explained below.

![Figure 1.3](image)

**Figure 1.3** (a) Phase equilibrium diagram in the In$_2$O$_3$–Ga$_2$O$_3$–ZnO system at 1350°C and (b) detailed phase equilibrium diagram near ZnO. Filled circles (●) and solid lines connecting two filled circles are a single phase. (a) Small letters (a to g) in the diagram represent a chemical composition as in the right of this figure. Regarding homologous compounds, the solid lines connecting In$_2$O$_3$\((\text{ZnO})_m\)–InGaO$_3$\((\text{ZnO})_m\)–In$_{1+x}$Ga$_{1-x}$O$_3$\((\text{ZnO})_m\) with the same \(m\) denote the solid-solution range. InGaO$_3$\((\text{ZnO})_m\) and InGaO$_3$\((\text{ZnO})_m\) have a hexagonal lattice, and Ga$_2$O$_3$\((\text{ZnO})_m\) has an orthorhombic lattice. **Source:** Adapted from [15]