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Survey Report on the Systemization of Technology

Systematic Survey of Innovation in Transparent Oxide Semiconductor "IGZO" for Next-Generation Thin-Film Transistors

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■ Abstract

Thin-film transistors (TFTs) have greatly contributed to the increase in the area of liquid crystal displays and organic electroluminescence displays. In recent years, amorphous silicon (a-Si:H) is being replaced by an oxide semiconductor known as "IGZO" (In-Ga-Zn-O) in TFTs. This is nothing less than a major revolution in the semiconductor field, where silicon has prospered. This revolution was brought about by two consecutive papers in ***Science*** (2003) and ***Nature*** (2004) published by the ERATO project group led by Prof. Hideo Hosono. The paper in ***Science*** discussed a homologous series of oxide crystals $InGaO_3(ZnO)_m$ (m = integer) with a layered structure that serve as the active layer of the transistor. The paper in ***Nature*** discussed an amorphous oxide semiconductor (a-IGZO, $InGaZnO_4$). a-IGZO TFTs in particular are easy to fabricate at low temperatures, are highly compatible with conventional silicon processes, have ten times higher electron mobility than amorphous silicon, and have much lower leakage currents. These are the reasons why IGZO has attracted attention from electronics manufacturers around the world. As a result, this discovery and invention has sparked a "game change" in the semiconductor field. The paper in ***Nature***, which is the source of this innovation, has become a landmark in both the fields of materials science and semiconductor transistors.

This systematic survey starts with historical changes in the research and development of well-known indium tin oxide (ITO) materials and multi-component transparent conductive oxides. From the author's point of view, this survey discusses the creation of new oxide semiconductors by Hideo Hosono, a professor at Tokyo Institute of Technology, who has always been up for a challenge and initiated innovation in this area since the mid-1990s. This survey also discusses the formulation of a "working hypothesis" logically derived from the results of several experiments by young researchers, as well as the workflow of the technology. In parallel with technology accumulation to epitaxially-grown single-crystal oxide thin films, this survey describes the detailed history of major discoveries and inventions that resulted from concrete validation of the "Hosono's working hypothesis" that even "amorphous" materials, which differ vastly from "crystals," can be endowed with electrical properties comparable to those of crystals. This survey deciphers how Hosono created "IGZO oxide semiconductors" as well as joint research with companies and research by individual project members while interweaving the author's speculations, theories, and imaginings.

During the era when silicon semiconductors flourished, even contamination with trace amounts of other elements were prohibited, so putting composite oxides containing three metals such as In, Ga, and Zn on the center stage of a new semiconductor industry was an arduous feat. This survey examines that difficulty from the perspective of materials science as well as efforts to apply for patents and acquire rights to the materials. In addition, this epoch of materials creation has encouraged researchers around the world. Currently, the technology is spreading in the field of high-definition flat panel displays as well as in a wide range of fields such as memory applications for electronics, X-ray detectors, and even biosensors. This survey will provide a brief overview of those fields of application.

a-IGZO semiconductors have created a large new technological platform based on two new cornerstones, materials science and device (TFT) technology. In March 2015, the Japan Academy awarded Hideo Hosono the Imperial Prize and the Japan Academy Prize for his achievements in "Study on creation and application of inorganic electro-active materials." In addition, he was also awarded the Japan Prize in 2016.

* As those who are familiar with materials research probably already know, Hideo Hosono is the pioneer of transparent oxide semiconductors (IGZO) for next-generation TFTs. In addition to creating these oxide semiconductors, the results of his outstanding research have had a profound impact on materials other than those covered here. The mineral $12CaO\ 7Al_2O_3$ (C12A7) is used in cement and was considered to be a typical insulator, but Hosono converted this material into a semiconductor, metal, and superconductor. This research led to the development of a new field called "electrides," in which electrons act as anions. In addition, Hosono has created a new layered oxychalcogenide

material that is a semiconductor. He also discovered an innovative iron-based layered oxypnictide superconductor ($LaFeAsO_{1-x}F_x$, Tc=26 K) that is unlikely to be an extension of the established BCS (Bardeen-Cooper-Schrieffer) theory in conventional metal-based superconductivity, causing a second “Woodstock of physics” in the superconducting materials field. Many of the results of his outstanding research are sometimes described as “discovering a new continent in materials exploration,” and they have opened a new chapter in solid state physics and created a new theory of materials science. I would like to add that Prof. Hideo Hosono remains one of the world's leading researchers in the field of materials science.

(∗This systematic survey report was revised in English in December 2024.)

■ Profile

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■ Contents

1 Introduction

Today, we are seeing a gradual increase in the number of families leading new lifestyles by installing thin liquid crystal displays (LCDs) with large screens and organic electroluminescence displays, also called organic light-emitting diodes (OLEDs), which use organic materials as light-emitting materials, in their living rooms. Thin film transistors (TFTs) using amorphous silicon (a-Si:H), which had previously boasted a stronghold in the industry, are now being widely replaced by TFTs using a new oxide semiconductor material called "IGZO", which allows each pixel of large screens to operate at a higher speed.

This systematic survey report will discuss how this oxide semiconductor material called IGZO was discovered and invented, what kind of a creative vision for material design was in the mind of Hideo Hosono, the pioneer of IGZO, during his many years of research history in functional oxide materials, what hints did he obtain from the numerous research results and findings of his predecessors, which he integrated into his vision, and how was he able to form a wonderful research team, thereby unraveling the dots and lines in the genealogy centering on the material technology of IGZO, with the author's deductions and speculations. In addition, I will report on the significance and possibilities that this discovery and invention brings to the academic community and the global industry, how the material is developing in reality, and the systematic survey of materials research centered on IGZO-based oxide semiconductor materials.

Research of functional oxides based in the electronics field began with the sudden boom in high-temperature superconducting materials from 1986 onward, which led to the discovery of the physical properties and characteristics of many new materials and the simultaneous emergence of a wide variety of cutting-edge technologies, such as precise structural analysis of crystals, oxygen partial pressure control, substrate topmost layer creation technology, and epitaxial single-crystal thin film fabrication technology. A material technology called ferroelectric nonvolatile memory emerged shortly after, which was also based on oxide materials with the same perovskite-type crystal structure as high-temperature superconducting materials, and it became a major technological trend on a global scale, so much so that the term "oxide electronics" was coined.

Until the mid-1990s, glass was generally associated with the concept of transparent oxides, and there were very few insulators with conductive properties, such as ITO (Indium-Tin-Oxide), which is made by adding a small amount of tin (Sn) to indium (In) oxide. This ITO is nothing but what is commonly referred to as a "transparent electrode". Apart from being used as electrode material for the above-mentioned thin LCD and OLED displays, this ITO thin film had come to be widely used as an electrode for photovoltaic cells, and materials with higher electrical conductivity were being sought.

Under such circumstances, a research team consisting of Hiroshi Kawazoe and Hideo Hosono from the Tokyo Institute of Technology, under their unique material design guidelines, discovered several new types of transparent conductive materials one after another from around the 1990s to the early 2000s and elucidated their mechanisms. The most notable among these research outcomes was the discovery of $CuAlO_2$, a p-type transparent conducting oxide, in 1997. Since only n-type oxides, with electrons as carriers, were known in the past, the discovery proved to be a trigger for the Hosono group to discover many new conductive oxides and n-type and p-type oxide semiconductors, which significantly accelerated research, including the creation of p-n junction diodes using only oxides, not to mention the attention from researchers around the world. Today, the term "oxide electronics" is used to collectively refer to the entire research on functional oxide materials with characteristic electronic properties, which has emerged since the 1990s, including a series of major research results of the Hosono group and the field of strongly correlated material science, also known as multiferroics, which has been garnering attention in recent years. The term "oxide electronics" was used for the first time in the world during an international conference under the strong guidance of Prof. Hideomi Koinuma and Prof. Hiroshi Kawazoe of the Tokyo Institute of Technology. After being used for the first time in 1995, the term has continued to evolve until "The 27th International Workshop on Oxide Electronics (iWOE27)" in Genoa, Italy, in the fall of 2021.

When we take a broader look at the Hosono Group's approach to materials research, their main focus was on transparent materials that are typically considered insulators, or in physical terms, materials with a wide energy gap (there was a time when such materials were referred to as "conductive insulators", a term coined by Hiroshi Kawazoe), and the major goal of the group in the early 1990s was to create new transparent conductive materials or semiconductor materials. The project launched based on 100% of Hosono's research strategy for materials creation is ERATO "HOSONO Transparent ElectroActive Materials Project" (October 1999 - September 2004), sponsored by the Japan Science and Technology Corporation (JST, currently the Japan Science and Technology Agency) under its Creative Science and Technology Promotion Project. "ERATO" is an abbreviation for "Exploratory Research for Advanced Technology". Hideo Hosono, who became the supervisor, demonstrated many outstanding research results to the world, such as the dramatic development of his materials design, the discovery of many new p-type oxide semiconductors and the creation of p-n heterojunctions and p-n homojunctions using carrier control technology and other technologies, and demonstration of diode characteristics

using only functional oxides (example, light emitting diode characteristics, etc.).

In the course of accumulating technology for a large number of such research findings, the group published a paper on a high-performance transparent field-effect transistor with an electron mobility of around 80 cm^2/Vs, using oxide crystals $InGaO_3(ZnO)_m$ (m = integer) that has a layered structure in homologous phases of In (Indium), -Ga (Gallium), -Zn (Zinc) and -O (Oxygen), in *Science*, in 2003. [*Science*, 300, 1269-1272 (2003).]

Subsequently, in 2004, the group published a paper in *Nature* on an amorphous oxide semiconductor TFT having an electron mobility of 6–9 cm^2/Vs, which is 10 times higher than that of amorphous silicon, using amorphous (non-crystalline) a-IGZO [=$InGaZnO_4$]-based oxide semiconductor as the active layer on top of a plastic film, demonstrating to the world that high-performance TFTs could be easily fabricated on flexible substrates, even at low temperatures suitable for manufacturing. [*Nature*, 432, 488-492 (2004).]

Generally, when crystalline silicon is amorphized, its electron mobility drops by 2 to 3 orders of magnitude, and there are concerns about significant degradation in its properties; however, the electron mobility of Hosono's amorphous transparent IGZO-based oxides drops by only 1 order of magnitude, and higher than expected values are maintained. IGZO has attracted high attention from relevant academic societies across the world and developers at electronics-related companies in Japan and overseas because of its advantage of low deposition temperature, potentially allowing a relatively easy introduction to the existing semiconductor processes, and because IGZO is expected to introduce new added value to the market, which is different from the conventional amorphous silicon TFTs, such as the feasibility of (1) a transparent device (2) a flexible device, and (3) clean normally-off function (no leakage currents with no voltage applied to the gate), due to which low energy consumption can be anticipated.

Several high-impact research results of JST-ERATO were directly passed down to ERATO-SORST "Functional Development and Application of Transparent Oxide Nanostructures", JST's development program (October 2004 - March 2010). "SORST" is an abbreviation for "Solution-Oriented Research for Science and Technology". Subsequent research and development were conducted in the ERATO-SORST program to improve the quality and stability of the transparent amorphous oxide semiconductor material discovered in ERATO and the thin transistor (Transparent Amorphous Oxide Semiconductors-TFT (TAOS-TFT)) using that material as the active layer (channel), which gave new perspectives to materials researchers and thin-film transistor researchers around the world. The numerous technical announcements by the Hosono Group served as a trigger for TFT-related research using oxide materials containing at least 2 of the 3 metallic elements, In, Ga, and Zn, as the active layer, such as research and development of two-dimensional stacking of channel layers in thin film transistors to increase electron mobility, and fabrication of TFTs using channel layers with fine homologous crystal particles preferentially oriented along the c-axis, at many other research institutions across the world. This is indeed a typical example of technological spillover. The starting point of this global challenge was indisputably the publication regarding amorphous oxide semiconductors in *Nature* in 2004 by Hideo Hosono's group.

After its publication in 2004, the IGZO-TFT technology attracted high attention from electronics-related companies around the world, including major electronics manufacturers in South Korea, because of its potential to create a new product value for smartphone screens and flexible displays without being limited to large LCD and OLED displays, not to mention further development of IGZO-based transparent oxide semiconductor material. As is well known, TFTs using this IGZO-based oxide semiconductor material are currently being adopted for driving many OLED displays. Recently, IGZO-based materials have also gained momentum for use in TFTs for memory applications and detectors for medical X-ray flat panels, and the discovery and invention of IGZO-based materials by Hosono et al. have made significant contributions and advancements in the electronics field in recent years, with focus on material technology.

In this systematic survey report, the technological history of amorphous IGZO-based oxide semiconductor materials and devices, which have established a new major platform, will be described in detail from Chapter 2 onward, including the author's perspective. A survey on their applications, developments, and spillover in the electronics industry in recent years will also be reported as a summary in Chapter 7.

2 History and Development of Transparent Conducting Oxides

2.1 Overview

Understanding the history and physical properties of transparent conducting oxides is essential to correctly understand the significance and importance of developing IGZO transparent amorphous oxide semiconductor materials used in thin film transistors. I will proceed with the discussion taking the example of ITO material, which is the most widely used transparent electrode in today's electronics field.

"ITO" is an abbreviation that stands for Indium Tin Oxide, which is a mixture of indium oxide (In_2O_3) and tin oxide (SnO_2). Usually, approximately 10% by weight of SnO_2 is added, which is a typical Transparent Conducting Oxide (TCO) substance and is still widely used in many devices today. Transmissivity is usually 80% or more in the visible light region, so thin films are almost colorless and transparent (ITO powder is light gray with a yellowish tinge). At the same time, electric resistance is extremely low at ~10^{-4} Ω·cm. Since this property approaches that of metals, it can act as an electrode, and the term transparent electrode often refers to the ITO material. The electron carrier density of ITO is in the range of 10^{20} cm^{-3} ~ 10^{21} cm^{-3}, depending on the amount of Sn added and the oxygen atmosphere during production. However, since the properties of materials with high carrier density approach that of metals, they also show reflection in the infrared region like metals. ITO is mostly used in the form of thin films, and general physical vapor deposition methods such as the sputtering deposition method or electron beam deposition method are often used as the film deposition method at present, while film forming methods such as spray pyrolysis using chemical solutions are also known from the past.

In recent years, ITO thin film is also a material that continues to be progressively researched as an optoelectronic material. Actual applications include flat-panel displays such as LCDs and OLEDs, electronic devices such as touch screens for mobile phones, transparent electrodes for thin-film solar cells, films for antistatic and electromagnetic interference, heat shielding films for windows of buildings and glass windows of freezers widely used in supermarkets, and other energy-related applications are also being developed.

By the way, Indium (In) is one of the rare metals, and its production is limited globally. Therefore, since the balance between demand and supply has to be considered, material development to reduce In content in the transparent electroconductive material is progressing, one such material is In_2O_3-ZnO based-material (IZO). In addition, as shown in Table 2.1, several transparent conducting oxides are used as practical materials, including AZO, where ZnO is doped with Al; GZO, where ZnO is doped with Ga; and FTO, where SnO_2 is doped with fluorine (F).

Table 2.1 Various transparent conductive oxides often used in practical applications

Materials and Compositions	Characteristics and Issues
ITO (Sn-doped In_2O_3)	・Rare Metal Utilization ・Low Temperature Deposition
AZO (Al-doped ZnO)	・Low Cost (Resource Free) ・Easy Wet Etching
GZO (Ga-doped ZnO)	・Low Temperature Deposition
ATO (Sb-doped SnO_2)	・Chemical Stability
FTO (F-doped SnO_2)	・Film Deposition at Relatively High Temperatures ・Wet Etching is Difficult

2.2 Research and Development of Transparent Conducting Oxides

2.2.1 ITO-Based Transparent Conducting Oxides

The history of research on transparent conducting oxides (TCOs) dates back more than 100 years, beginning with Franz Streintz's evaluation of the conductivity of cadmium oxide (CdO) in 1902[1]. In this case, Franz Straintz used compressed powder pellets for his evaluation. Later, in 1907, it was studied[3] in more detail by Karl Bädeker[2], shown in Fig. 2.1. In recent years, a paper by Marius Grundmann, a professor at Leipzig University in Germany, has credited Karl Bädeker as the discoverer of transparent conducting oxides (TCO)[4].

Fig. 2.1 Prof. Karl Bädeker[2]

Thus, for about half a century from around 1900, materials containing cadmium (Cd) element were very frequently used as constituent materials of semiconductors. However, since cadmium, a toxic substance, is used in the matrix composition, its use is currently limited to special purposes.

So where did ITO, the most widely used transparent conducting oxide material today, originate? Among transparent conducting oxides, I would like to give an overview of the history of the invention of the so-called ITO-based transparent conducting oxides, which are SnO_2-based or Indium-Tin-Oxide, a mixture of SnO_2 and In_2O_3.

According to a paper[5] by Asakuni Ishikawa of Mazda Research Institute, Tokyo Shibaura Electric and a paper[6] by Tadayoshi Inui et al. of Kyushu Institute of Technology, the first patent (US Patent 2118795)[7] was filed by J. T. Littleton of Corning Glass Works in the United States for the preparation of iridescent coating (~conductive coatings) using tin(IV) chloride ($SnCl_4$) for antistatic purposes. An excerpt of the main part of the drawing used in that patent is shown in Fig. 2.2.

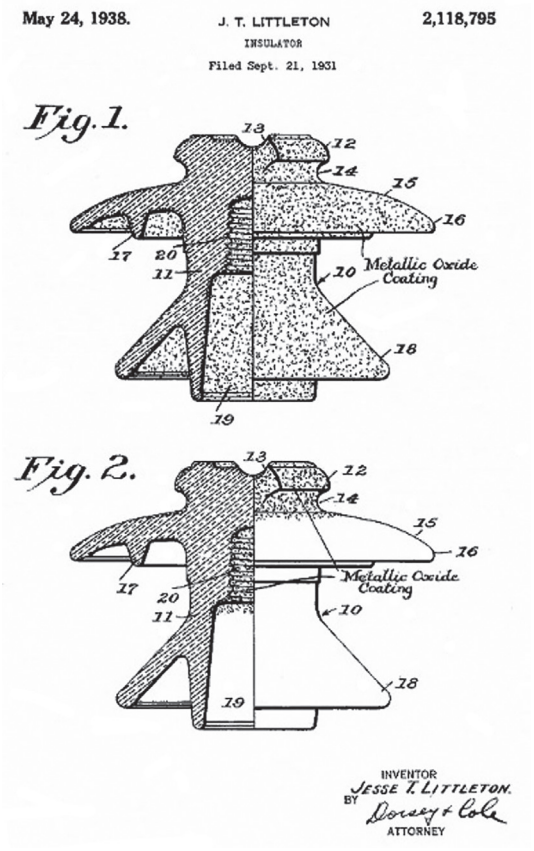

Fig. 2.2 Excerpt from US Patent 2118795[7]

Subsequently, the foundation for Corning's research into transparent conductive thin films was established around 1950 through progressive research by J. M. Mochel and his colleagues from Corning. Fig. 2.3 shows some of the drawings used in a patent (US Patent 2429420)[8] filed by H. A. McMaster of Libbey-Owens-Ford Glass Company.

In parallel with Corning's development, Pittsburgh Plate Glass Co. in the US also succeeded in increasing the film's conductivity by adding an organic reducing agent and commercializing it as NESA film. For a time, the term "NESA film" became synonymous with transparent electrodes.

In 1954, Georg Rupprecht measured the conductivity of films deposited with indium oxide and reported that it was sensitive to oxygen partial pressure[9]. This paper is considered to be the earliest paper on In_2O_3-based conductive oxides.

Here, I will mention the detailed research report by Takako Honjo. Honjo has published a detailed research report on the history of science, focusing on Yoshiyuki Katsube and his wife, Shizuko Katsube, who significantly contributed to the

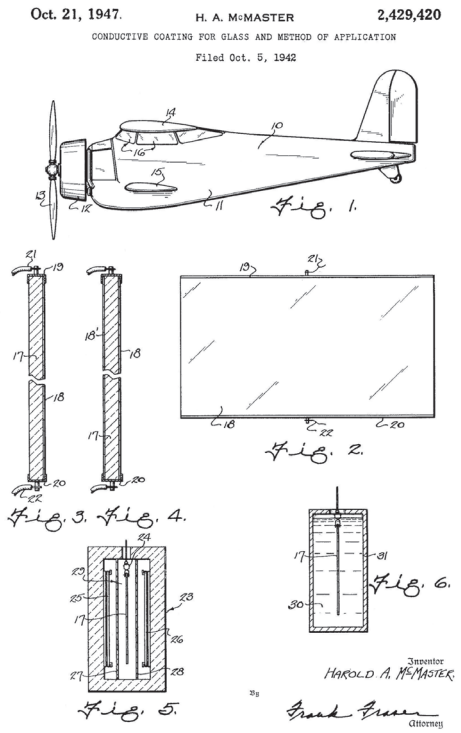

Fig. 2.3 Excerpt from US Patent 2429420[8]

development of ITO materials in Japan[10]. In 1969, Yoshiyuki Katsube and Shizuko Katsube of the Ministry of Trade and Industry, Agency of Industrial Science and Technology, and the Osaka Industrial Research Institute (abbreviated as OIRI, now Kansai Center of National Institute of Advanced Industrial Science and Technology) in an invention[11] titled "Production method for high-performance conducting films based on indium oxide" claimed that the resistance value is lowest when the addition amount of SnO_2 to In_2O_3 is near 5% by weight. They reported details of the significant contributions made to the subsequent development of businesses such as liquid crystal electronics elements[10]. The research results of Yoshiyuki Katsube and his wife, Shizuko Katsube, from OIRI, have led to the registration of several other patents in addition to the above, and their steady research[12)-15)] initiatives are considered to be an extremely significant achievement in the early days of ITO-based transparent conducting films.

From the late 1960s to the 1970s, researchers from numerous companies were involved in researching and developing this transparent conductive film, and several papers have been published. For example, research by Hori et al.[16] of Furukawa Electric Co., Ltd., using the vacuum deposition method, a series of film formation studies using organic tin salts as raw material by Kawamata et al.[17)-21)] from National Institute of Technology, Oyama College, consideration of optical properties of SnO_2, which has attracted attention as a transparent electrode, by Nagasawa[22] of Matsushita Electric Industrial Co., Ltd., and evaluation of the characteristics of NESA film (SnO_2 film) as an electrode by Kitaoji et al.[23] from Fujitsu Laboratories. Sharp appears to have been actively conducting

research and development for the commercial applications of transparent conducting film from an early stage and has published technical reports on their application in electronic display elements such as calculators to thin displays[24]. In addition, Nagatomo et al.[25] of Shibaura Institute of Technology have evaluated the characteristics of tin oxide films using the spray method, report by Omoto[26] on thin film preparation methods for In_2O_3 and SnO_2, Mizuhashi of Asahi Glass has conducted detailed experiments on carrier doping and electrical properties of SnO_2 films, In_2O_3 films, and ITO films, which are the base materials for transparent conducting oxides, and published comprehensive reports[27), 28]. Ten years later, Haranou et al.[29] from the same company, Asahi Glass, carefully summarized the fundamental properties of ITO, and after 2000, Mizuhashi again published an ITO-related report[30]. A group from the Indian Institute of Technology has conducted a more comprehensive review[31].

Subsequently, in 1994, R. J. Cava et al. of AT&T Bell Laboratories took up $GaInO_3$, having a β-Ga_2O_3 structure, as a new transparent conducting oxide with higher transmittance than ITO film in the green to blue wavelength range and reported improvements in conductivity by doping In with Sn, doping Ga with Ge, and introducing oxygen defects[32), 33]. Furthermore, the same group researched thin films of Zn-In-O-based transparent conducting oxides. In addition to demonstrating good characteristics in the visible and infrared regions, the group also mentioned the doping effects of adding elements such as Al, Ga, and Ge and conducted pioneering research in this field[34].

Around the same time as the publication of the paper by Cava et al., an important report was published by a group led by Shigesato et al., who was then affiliated with Asahi Glass in Japan. They reported on the heteroepitaxial growth of ITO thin films using YSZ (Yttria-Stabilized Zirconia) single-crystal substrates. Epitaxial growth of thin films is a typical technology developed during the boom of research into high-temperature superconducting oxides, and this technology was quickly applied to ITO thin films[35)-37]. Shortly after this, the reactive solid-phase epitaxial growth method was invented by Ohta et al. of the Hosono group, which will be discussed later, and reflecting on this period in this context is very interesting.

In addition, one of the characteristic methods to prepare oxides is the sol-gel method. A group[38)-40] from Gifu University has published several reports on producing ITO-based transparent conducting films from a solution process using this method. Furthermore, Yoshikawa et al.[41] focused on ZnO-In_2O_3-based transparent electroconductive materials from the perspective of synthesizing from the liquid phase, and reported a process that involves adding citric acid as a gelator to a mixed aqueous solution of zinc nitrate and indium nitrate.

In this way, transparent conducting films have been the subject of vigorous research since the 1960s, and their applications have been developed in parallel, one after another, due to their usefulness, making them materials that are directly linked to industrial applications. In the second half of the 1970s, research and development of this material was carried out actively as a transparent electrode for amorphous silicon thin-film solar cells. From the 1980s, it was used for flat-panel displays, mainly liquid crystal displays and as a transparent electrode for touch panels. However, detailed procedures and particular conditions (substrate temperature, plasma conditions in the chamber, adjustment and control of oxygen partial pressure, post-annealing conditions, etc.) for film formation are rarely disclosed as they are proprietary data within each company.

While the types of transparent conducting oxide (TCO) materials vary depending on the application, they have evolved from SnO_2-based, to In_2O_3 (ITO)-based, and ZnO-based and further to multi-component TCOs in materials research. Even today, many materials are continuously being developed and researched. The details are meticulously described in the commentary by Tadatsugu Minami, a professor of Kanazawa Institute of Technology, who has published many research papers in the field of oxide materials for transparent electrodes[42].

Volume 25, Issue 8 of the MRS Bulletin magazine in 2000 featured transparent conducting oxides and was planned and authored by world-renowned researchers[43)-49]. The magazine includes contributions from eminent researchers of the world in 2000, including papers by Hiroshi Kawazoe and Hideo Hosono[45] and Tadatsugu Minami[46].

In Japan, Tosoh Corporation is conducting experiments on the Sn content dependency, etc., intending to commercialize transparent conducting films, and has reported the various characteristics in a compiled format[50]. Additionally, in 2004, a team from Northwestern University reported on the historical evolution and interesting classification of transparent conducting oxides (TCOs)[51]. They are classified and organized into 4 basic families: oxides with tetrahedrally-coordinated cations (ZnO, etc.), oxides with octahedrally-coordinated cations (multi-element oxides such as In_2O_3, SnO_2, ITO, etc.), oxides with linearly-coordinated cations ($CuAlO_2$, $SrCu_2O_2$, etc.), and electride oxide groups with cage structures ($12CaO{\cdot}7Al_2O_3$, etc.). Furthermore, in 2005, the journal published by the Optical Society of Japan, Vol. 34, No. 7 (July 2005), featured the advancements in the research of transparent conducting oxides[42), 52), 53)-57].

Tadatsugu Minami, who is renowned in this field, has been actively conducting research on thin-film technology for transparent conducting oxides for many years since the 1990s and has compiled many of his research results to date in several review articles, including those mentioned above, primarily in OYO-BUTURI, the journal published by the japan society of applied physics[58)-61]. In particular, Minami reported that the band gap, work function, etc., can be controlled from electrical and optical perspectives by adjusting multi-element transparent conducting films from various angles, clearly demonstrating the importance of developing applications suited to each[62]. In addition, in response to the historical evolution of

TCOs, Minami has summarized various properties, such as SnO_2-based, In_2O_3-based and its doped materials, complex oxides and multi-element materials containing cadmium (Cd), and the stability of material systems associated with doped elements[46), 63)].

On the other hand, contrary to the growing need for transparent electrodes for optoelectronic devices, there is a need to explore alternatives for ITO materials, which use indium (In) as the main component and are becoming a concern due to their harmfulness. Minami has published several papers identifying ZnO-based transparent conducting oxides, particularly Al-doped and Ga-doped ZnO (AZO and GZO) transparent conducting oxides, as promising candidates and has also discussed improvements in large-area technologies using sputtering and vacuum evaporation techniques[64)-69)]. Concerning the pending issue of Indium, the January 2007 issue of CERAMICS JAPAN (Bulletin of the Ceramic Society of Japan), Vol. 42, featured a sub-theme on "An Alternative Transparent Conducting Oxides to Indium Tin Oxide", with contributions from experts in various fields[70)-73), 30), 74)-76)].

After 2005, Yuuzou Shigesato et al.[77)] of Aoyama Gakuin University achieved a resistivity = 3.39x 10^{-4} Ω·cm with a carrier concentration = 10 ~ 20 cm^{-3} in the In-Zn-O system by doping Sn, Al or F and introducing oxygen defects by hydrogen reduction atmosphere treatment. In addition, reports[78)], [79)] from personnel of Asahi Glass, Niki et al. of the National Institute of Advanced Industrial Science and Technology (AIST)[80)], and Shiratsuchi[81)] of Kyushu Institute of Technology have written about the development status and outlook for transparent conducting film from their respective perspectives. Furthermore, Koida et al.[82)] of AIST have reported on a newly developed In_2O_3-based high-mobility transparent conductive film. In addition, Sato et al. of Kochi University of Technology have reported on research trends regarding transparent conductive films[83)], and ULVAC[84)], a company well-known for its vacuum deposition equipment, has reported on the relationship between the deposition conditions and characteristics of ITO films.

Furthermore, 2 representative examples of review articles from a global perspective include those by Andreas Stadler[85)] and Elvira Fortunato et al.[86)]. Recently, a paper has also been published on the material search for transparent conducting oxides using computers[87)] and a comprehensive report on transparent conducting materials with the crystal structure of perovskite-type oxides, which are known for ferroelectrics and high-temperature superconductors[88)]. Material development from the broad perspective of oxide electronics is expected to continue progressing in the future. According to a report by Tadatsugu Minami[42)], as shown in Fig. 2.4, the resistivity of transparent conducting oxides has gradually decreased over the years, reaching a point where it is less than 10^{-4} Ω·cm.

As mentioned above, many research papers have been published on ITO-based transparent conductive materials alone covering all of them in this research report is impossible. I request your understanding in this regard.

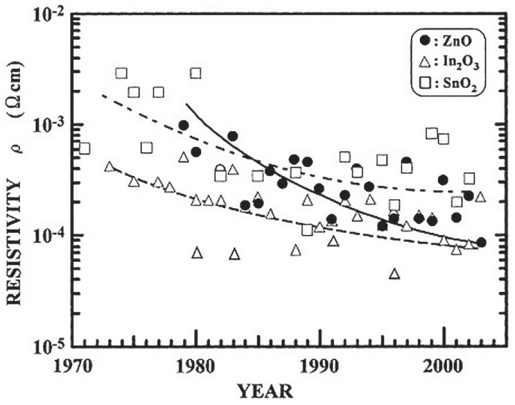

Fig. 2.4 Historical change of resistivity of transparent conducting oxides (Three main types: ZnO-based: ●, In_2O_3-based: △, SnO_2-based □)
(Reprinted from reference (42) with permission of "KOGAKU" [*Japanese Journal of Optics*])

2.2.2 Multi-Component Transparent Conducting Oxides

In the field of transparent conducting oxides, systems containing 3 or more metallic elements, such as ZnO-In_2O_3-SnO_2 (ZITO) and Ga_2O_3-In_2O_3-SnO_2 (GITO) based materials, are generally called multi-element oxides. Research on multi-element transparent conducting oxides began around 1995.

After the paper[32), 33)] on $GaInO_3$ by Cava et al. of Bell Laboratories in 1994, as described in the previous section, Cava et al. then published a paper[34)] on Zn-In-O in 1995. At the same time, the research results of Tadatsugu Minami of Kanazawa Institute of Technology were successively published[89)-92)]. Multi-element oxides often contain metallic elements such as Zn, In, Sn, and Ga, but as with Cava et al., the paper by Minami was initially published focusing on binary metal-based thin film preparation.

These successive research reports led to vigorous exploratory research to add one more metallic element to the list, which began around 1997 led by Kenneth R. Poeppelmeier's group at Northwestern University in the U.S. Shortly after the start of his research, Poeppelmeier conducted joint research with Toshihiro Moriga of Tokushima University, leading to the publication of many research papers and thus making Poeppelmeier one of the world's foremost researchers of transparent conducting oxides even today. Poeppelmeier's group has produced several research results on various multi-element oxide materials from multiple perspectives, including structure chemistry, electrical conductivity, and optical properties, such as the following. [Numbers in parentheses ( ) are reference numbers]

- ◆ Overview (published in 2000): (47)
- ◆ ZnO-In_2O_3-SnO_2 (ZITO): (93), (94), (95), (96), (97), (98), (99), (100)
- ◆ Ga_2O_3-In_2O_3-SnO_2 (GITO): (101), (102), (103), (104), (105), (106), (107)
- ◆ Homologous phase $In_2O_3(ZnO)_m$ and $InGaO_3(ZnO)_m$: (108), (109)

Column: The Nature of ITO Transparent Conducting Oxides —from the Author's Perspective—

○ ITO[1] is a material where 5-10% of Sn (tetravalent) is solid-solution substituted into the In (trivalent) site of In_2O_3 (which has a cubic bixbyite type crystal structure, with $E_g \sim 3.7$eV), doping it with electron carriers, and many fundamental studies have been conducted to date[2)-24)]. If the electron carrier concentration exceeds $10^{18}/cm^3$, the optical energy gap is apparently widened, as shown in Fig. 2.5. (shift amount $\Delta E_{B\text{-}M} \sim 0.6$ eV). This is called the Moss-Burstein effect[25), 26)].

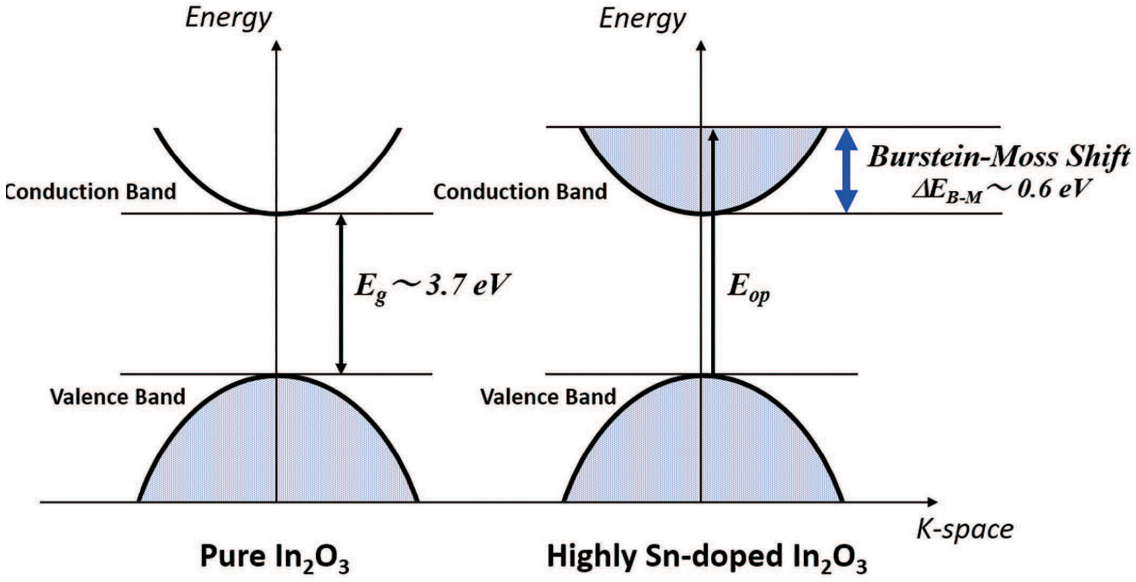

Fig 2.5 Change in electronic state due to Sn-doping into In_2O_3 (Moss-Burstein effect)
In_2O_3 is said to be an indirect transition semiconductor, but for the sake of clarity, the band structure is briefly depicted here as a direct transition type.

At the same time, a sea of electrons is formed at the bottom of the conduction band, and the Fermi level enters the conduction band, resulting in a metallic state. Materials formed in this way are called degenerate semiconductors, and their resistivity is either almost independent of temperature or tends to increase slightly with increasing temperature, like a metal. It is this substance, ITO, in a degenerate semiconductor state, commonly used for transparent electrodes, etc.

○ However, there are significant differences compared to metals. It is not simply a metal that is transparent in the visible range. In metals such as gold, silver, and copper, the electron carrier density is $10^{22}/cm^3$ or more. Hence, the plasma frequency ω_p is in the ultraviolet to the visible region, and transparency in the visible light region is lost. However, in the case of transparent conducting oxides such as ITO, which do not have a carrier density as high as metals, the plasma frequency ω_p is often located not in the visible region but in the immediately adjacent near-infrared region (wavelength 1-2 μm). Strong plasma absorption occurs in this wavelength region, exhibiting high reflection characteristics in longer wavelength regions. That is, since ITO has a wide band gap in the visible light region, it is almost transparent, although there is a slight effect by the tail of plasma absorption. Therefore, it is called a transparent conducting oxide.

○ In theory, adjusting the plasma frequency ω_p of TCO is possible by controlling the carrier density. This special feature of transparent conducting oxides cannot be achieved with ordinary metals. ITO can be truly called a "gift from heaven." Transparent conducting oxides such as ITO are extremely rare substances that have the potential to be designed into materials that transmit wavelengths in the visible range of sunlight and reflect (heat shield) wavelengths in the infrared region. In other words, a wide-gap semiconductor will be formed if the carrier density due to doping is small, and almost no plasma reflection will occur in the infrared region. However, if the carrier density is high, the material will be in a metallic state known as a degenerate semiconductor, causing plasma reflection in the infrared region, thereby improving the light shielding properties[27)].

○ However, even if designed to block electromagnetic waves in the infrared region by increasing the carrier density

through doping with different valence metals or oxygen defects, maintaining the transmittance in the visible light region at the same level as the transmittance when the carrier density is low is often practically very difficult. There is often a trade-off between increasing transparency in the visible region and reflection in the infrared region. If this can be solved in the future, it could be a clue to solving energy problems. I look forward to seeing further developments.

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◆ Ga_2O_3-SnO_2-ZnO (GTZO): (110)
◆ Co-doping of In_2O_3 with divalent (Zn) and tetravalent (Sn, Ge): (111), (112), (113), (114), (115)
◆ ITO-based: (116), (117)
◆ Cd-In-Sn-O: (118), (119), (120), (121), (122)

A carefully organized report detailing the study of Zn-In-Sn-O in ZITO-based materials[93] shows that as the amount of In increases, (1) the lattice constant increases, (2) the optical band gap decreases, (3) the electrical conductivity increases, and (4) the optical transmittance decreases. In addition, the identification of a wide range of crystalline phases in the triangular phase diagram of Zn-In-Sn-Oxide and their correlation with various properties were published in another research paper[96]. A simplified triangular phase diagram of In-Zn-Sn oxide is shown in Fig. 2.6. The left side of In-ZnOxide in the triangular phase diagram signifies that a series of oxides with a homologous composition is formed. While the solid line section inside the triangular phase diagram denotes the region where a solid solution is formed.

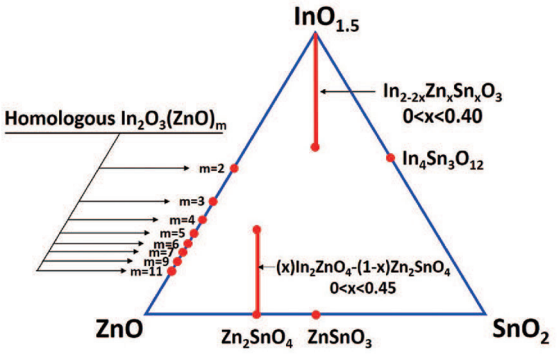

Fig. 2.6 Triangular phase diagram of In-Zn-Sn oxide system.
(Created by the author based on the triangular phase diagram in reference (96), with emphasis on the solid solution region.)

The series seen in the In-Zn-O system on the left side of the triangular phase diagram is a group of materials called a homologous system, expressed by the general formula $In_2O_3(ZnO)_m$, and is explained in the next section.

2.2.3 Homologous Transparent Conducting Oxides

(1) The Dawn of Homologous Oxide Discovery

Thus, while research on transparent conducting oxides has shifted from ITO to multi-element oxides, including the study of homologous oxides with unique stacked structures, as discussed in the papers co-authored by Poeppelmeier and Moriga[108), 109)], since basic research on the crystal structure chemistry of these materials has been conducted well before 1990, we will begin by first reviewing the history of material research.

The first person in the world to report that the In-Zn-O phase has a homologous oxide group was Horst Kasper, a German inorganic chemist, in 1967[123)]. In this paper, the author has pointed out specifically the existence of an oxide that can be expressed by the general formula $Zn_kIn_2O_{3+k}$ and reported that its lattice constant changes sequentially and regularly for the series k = 2, 3, 4, 5, and 7. Based on the results of this research, the origin of the study of homologous oxides can be attributed to Kasper's paper on the In-Zn-O system[123)].

Incidentally, since studies have been published on the synthesis and crystalline phases of complex oxides with ordinary In as the main component rather than of homologous materials, the author would like to mention this as important relevant information[124), 125)]. In particular, the paper in reference (125) is considered the earliest research paper on M(II)M(III) InO_4 [where M(II) = Mg, Mn, Co, Cu, Zn, Cd, and M(III) = Al, Ga], a group of oxides with a spinel-type crystal structure, including $MgIn_2O_4$, $CdIn_2O_4$, $MgGa_2O_4$, $MgGaInO_4$, $CuAlInO_4$ and $MgAlInO_4$. This paper mentioned that $InGaZnO_4$, which contains In, Ga, and Zn, was synthesized at 1290°C and is classified as a hexagonal system, the same as $CuAlInO_4$, with lattice constants a = 0.3298 nm and c = 2.613 nm. This paper is probably the first to mention the material $InGaZnO_4$ in a research paper and to provide information on the crystal structure, etc., of the material and its synthesis conditions.

Since the publication of Kasper's paper[123)] mentioned above, as important research results on In-based homologous oxides include the observation of the earliest TEM lattice images of $In_2O_3(ZnO)_{10}$ crystals and the intergrowth growth by P. J. Cannard et al. in the UK[126)].

(2) Basic Research Results on Crystal Structure Chemistry of Homologous Oxides led by Noboru Kimizuka of the National Institute for Research in Inorganic Materials

Except for Kasper and Canard, who achieved the earliest research results, it was a group led by Noboru Kimizuka at the then National Institute for Research in Inorganic Materials (now National Institute for Materials Science (NIMS)) of the Science and Technology Agency that has continuously promoted systematic research on In-based homologous oxides. The research on the formation of materials has been conducted precisely, including thermodynamic considerations, and basic research from the viewpoint of crystal structure chemistry of materials has been vigorously promoted and has been leaving behind a vast amount of research results. Noboru Kimizuka has made an extremely significant contribution to the field of homologous oxides. A list of the major papers published by Kimizuka et al. up to about 2004 is shown in Table 2.2. The left column of this table is classified as a group of magnetic-related materials containing mainly Fe, and the right column as a group of homologous materials containing mainly In.

Noboru Kimizuka, who has been collaborating with Takashi Katsura, a professor of Tokyo Institute of Technology, since around 1974, has focused on the study of phase equilibrium of Fe-based complex oxides such as Yb-Fe-O and Lu-Fe-O under high temperatures, creating several new materials. With due consideration given to the possibility of fluctuations in metal valence, Kimizuka conducted research synthesizing various materials through a carefully controlled process in which the oxygen partial pressure is adjusted during synthesis

Table 2.2 A list of basic research results on crystal structure chemistry of homologous oxides led by Noboru Kimizuka.

Research on Crystal Structure and Magnetism of Rare Earth-Iron Multiple Oxides	Fundamental Research on Crystal Structure Chemistry of In-Based Homologous Oxides
○$Yb_2Fe_3O_7$ and $Lu_2Fe_3O_7$ Solid State Communications, 15, <7>, 1199-1201 (1974). ○$A^{3+}Fe_2O_4$ (A = Ho, Er, Tm, Yb, and Lu) Solid State Communications, 15, <8>, 1321-1323 (1974). ○$YbFe_2O_4$ Z. Kristallogr., 141, 314-320 (1975). ○$YFeO_3$, $Y_3Fe_5O_{12}$, YFe_2O_4 J. Solid State Chem., 13, <3>, 176-181 (1975). ○$YbFe_2O_4$, $Yb_2Fe_3O_7$, $YbFeO_3$, $Yb_3Fe_5O_{12}$ J. Solid State Chem., 15, <2>, 151-157 (1975). ○$Yb_3Fe_4O_{10}$, $Yb_4Fe_5O_{13}$ Acta Crystallogr., B 32, 1620-1621 (1976). ○$Yb_2Fe_3O_7$ Z. Kristallogr., 143, 278-284 (1976). ○YFe_2O_4 Mater. Res. Bull., 11, <6>, 637-643 (1976). ○Fe-Ln-O系 J. Solid State Chem., 23, <1–2>, 43-57 (1978). ○YFe_2O_4 J. Phys. Soc. Jpn., 47, 1369-1370 (1979). J. Phys. Soc. Jpn., 47, 1737-1738 (1979). Solid State Communications, 32, <11>, 1065-1068 (1979). ○$Yb_3Fe_4O_{10}$ Acta Crystallogr., B 35, 561-564 (1979). ○GeO_2-FeO-Fe_2O_3 system, Fe-Ge-O系 J. Solid State Chem., 38, <1>, 82-86 (1981). J. 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Solid State Chem., 49, <1>, 65-76 (1983). ○YFe_2O_4, $YbFe_2O_4$ J. Phys. Soc. Jpn., 53, 2688-2696 (1984). J. Cryst. Soc. Jpn., 26, 334-343 (1984). [in Japanese] ○$RFeMO_4$ [M=Mn, Co] J. Phys. Soc. Jpn., 53, 4113-4116 (1984). ○$LuFe_2O_4$ J. Phys. Soc. Jpn., 56, 3746-3747 (1987). ○YFe_2O_4, $YbFe_2O_4$, $LuFe_2O_4$ Physica B: Condensed Matter, 155, <1–3>, 307-310 (1989). ○ $LuFe_2O_4$, $LuFeCoO_4$, $YbFeMgO_4$ J. Crystal Growth, 102, <3>, 398-400 (1990). ○$YbMnO_3$ Acta Crystallogr., C 47, 423-424 (1991). ○$LuFeO_3(ZnO)_m$ (m=1, 4, 5 and 6) Acta Crystallogr., C 50, 332-336 (1994). ○$Fe_2O_3(ZnO)_m$ J. Solid State Chem., 142, <1>, 174-179 (1999). ○$ErFeMnO_4$, $YbFeMnO_4$ J. Alloys and Compounds, 313, <1-2>, 59-64 (2000). Acta. Crystallogr., B 56, 805-810 (2000).	○In_2O_3-A_2O_3-BO [A: Fe, Ga / B=Cu, Co] ex.$InGaCuO_4$, $InGaCoO_4$ J. Solid State Chem., 53, <2>, 217-226 (1984). ◎$InGaFeO_4$, $InGaNiO_4$, $InGaZnO_4$, $InGaMgO_4$, $InAlCuO_4$, $ScGaZnO_4$ et.al. **J. Solid State Chem., 60, <3>, 382-384 (1985).** :::::::::::::::::::★ ○$ScZnGaO_4$, $InZnGaO_4$, $InMgGaO_4$ [Luminescence] Mater. Res. Bull., 21, <9>, 1057-1062 (1986). ◎Homologous-$InFeO_3(ZnO)_m$ (m=1–9) + TEM of $InGaO_3(ZnO)_5$ **J. Solid State Chem., 74, <1>, 98-109 (1988).** :::::::::::::::::::★ ○$RAO_3(MO)_n$ [R = Sc, In, Y, Ln / A=Fe, Ga, Cr, Al, M=Mg, Mn, Fe, Co, Ni, Zn, Cd] J. Solid State Chem., 78, <1>, 98-107 (1989). ○$InAO_3(MO)_m$ [A=In, Fe, Ga, Cr, Al / M=Mg, Mn, Co, Fe, Zn] J. Solid State Chem., 81, <1>, 70-77 (1989). ○In_2O_3-Fe_2ZnO_4-ZnO system, $In_{1+x}Fe_{1-x}O_3(ZnO)_m$ et al. J. Solid State Chem., 86, <1>, 16-40 (1990). ○In_2O_3-A_2BO_4-BO [A=Fe, Ga, Cr / B=Mg, Co, Ni, Cu, Zn] , $InGaO_3(MgO)_m$ J. Solid State Chem., 87, <2>, 449-455 (1990). ◎Homologous-$InGaO_3(ZnO)_m$, In1-xGa1+xO3(ZnO)m, [m=1-13] **J. Solid State Chem., 93, <2>, 298-315 (1991).** :::::::::::::::::::★ ○$RMO_3(M'O)_m$ [R=Sc, In, Y, Ln (Ho~Lu) / M=Fe, Ga, Al / M′=Mg, Mn, Fe, Co, Cu, Zn] J. Solid State Chem., 99, <2>, 243-257 (1992). ○Homologous-$InFeO_3(ZnO)_m$, $Fe_2O_3(ZnO)_m$ J. So1id State Chem., 103, <2>, 394-402 (1993). ○$InMO_3(ZnO)_m$, $M_2O_3(ZnO)_m$ [M=Fe, Ga, Al] J. Alloys and Compounds, 192, <1-2>, 105-107 (1993). ○Homologous-$InAlO_3(ZnO)_m$, $In_{1+x}Al_{1-x}O_3(ZnO)_m$ [m≧2] J. So1id State Chem., 105, <2>, 535-549 (1993). ○Homologous-In(In,Fe,Ga,Al)$O_3(ZnO)_m$ Kotai Butsuri, 28, <5>, 317-327 (1993). [in Japanese] ○Homologous-$InFeO_3(ZnO)_m$ J. Electron Microscopy, 43, <3>, 146-150 (1994). ◎Homologous-$In_2O_3(ZnO)_m$, $InGaO_3(ZnO)_m$, $Ga_2O_3(ZnO)_m$ **J. Solid State Chem., 116, <1>, 170-178 (1995).** :::::::::::::::::::★ ○Homologous-$ln_2O_3(Zn0)_m$ J. Electron Microscopy, 46, <2>, 119–127 (1997). ◎Homologous-$InMO_3(ZnO)_m$ [M=In, Ga] + Modulation **J. Solid State Chem., 139, <2>, 347-355 (1998).** :::::::::::::::::::★ ○In_2O_3-TiO_2-Fe_2O_3 system J. Solid State Chem., 144, <1>, 91-99 (1999). ○$In_3Ti_2AO_{10}$, $In_6Ti_6BO_{22}$ [A=Al, Cr, Mn, Fe, Ga / B=Mg, Mn, Co, Ni, Cu, Zn] J. Solid State Chem., 147, <2>, 438-449 (1999). ○$InFe_{0.33}Ti_{0.67}O_{3.33}$ Acta. Crystallogr., C 55, 1755–1757 (1999). ○Homologous-$Ga_2O_3(ZnO)_m$ Acta Crystallogr., B 55, 355-362 (1999). ○In_2O_3–TiO_2–MgO system J. Solid State Chem., 150, <2>, 276-280 (2000). ○Spinel-Zn_2TiO_4 Mater. Res. Bull., 35, <3>, 351-358 (2000). ○$InMO_3(ZnO)_m$ [M=Al, In / m=integer] Micron, 31, <5>, 543-550 (2000). ○$InFeO_3$-$In_2Ti_2O_7$ system Chem. Mater. 12, <8>, 2244–2249 (2000). ○Homologous-$RMO_3(ZnO)_m$ [R=In, Fe / M=In, Fe, Ga, Al] Kotai Butsuri、35, <1>, 23-32 (2000). [in Japanese] ○$In(Fe_{1-x}Ti_x)O_{3+x/2}$, $InCr_{1-x}Ti_xO_{3+x/2}$ J. Solid State Chem., 157, <1>, 13-22 (2001). J. Solid State Chem., 163, <2>, 455-458 (2002). J. Cryst. Soc. Jpn., 45, 124-130 (2003). [in Japanese] J. Solid State Chem., 177, <8>, 2644-2648 (2004). :::::★: Papers considered particularly important in this systematic survey when looking back at homologous $InGaO_3(ZnO)_m$ single-crystal transistor technology in *Science* (2003).

Column: Homologous Phases and Similar Compounds

The original meaning of the word homologous is “same series” or “same family”. It is a generic term used to refer to a group of compounds in which the chemical composition formula of a compound can be concisely expressed using n, where n is a natural number.

The transparent conducting oxides discussed in this chapter are often employed for their crystal structures, as exemplified by the homologous oxide $LuFeO_3(ZnO)_m$ illustrated in the following Fig. 2.7. Of course, $InGaO_3(ZnO)_m$ too is one of the groups with similar homologous crystal structure.

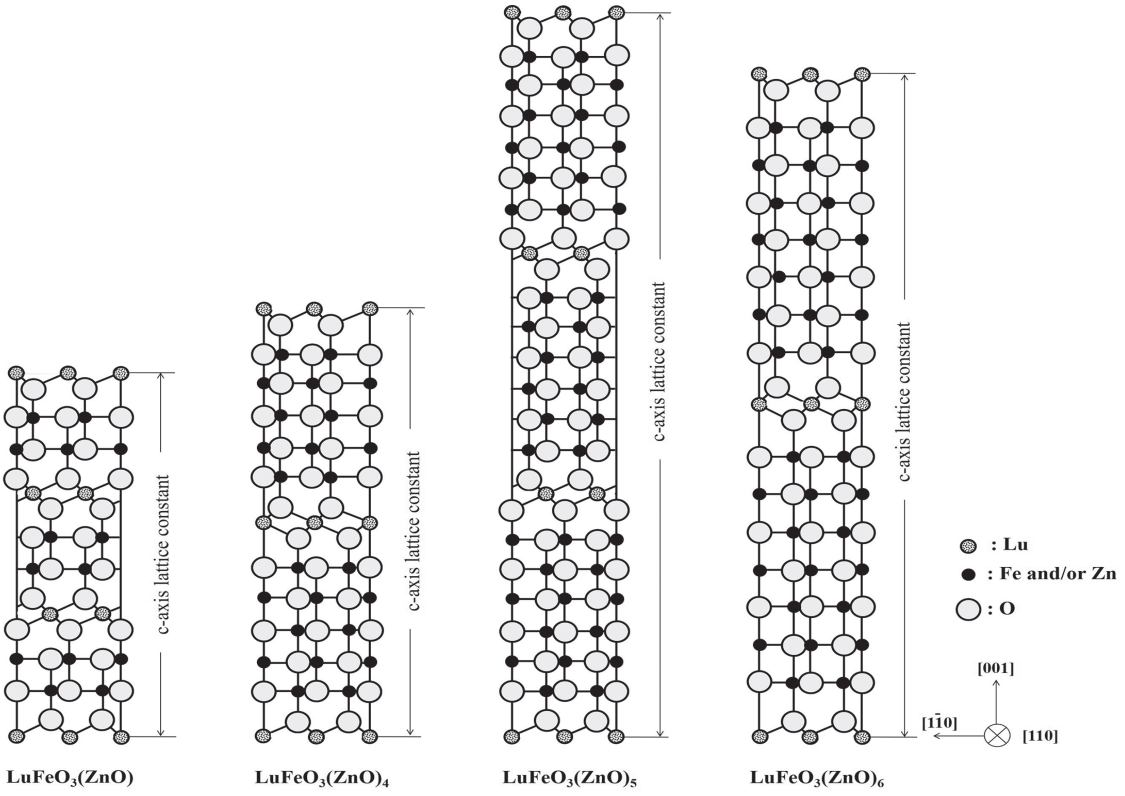

Fig. 2.7 Simplified-drawn crystal structure of homologous $LuFeO_3(ZnO)_m$. (from left to right, m=1, 4, 5. 6)
To facilitate understanding of how the c-axis lattice constant extends in proportion to the increase in m value, the crystal structure is depicted in a slightly different way than the actual bonding direction. The author hopes readers will understand this point. When m is odd, the crystal is $R\bar{3}_m$ symmetry, and when m is even, it is $P6_3/mmc$ one. For this reason, we must note that the c-axis length is changed in even-odd alternation. (The above crystal structure image was prepared by the author with reference to papers by Kimizuka et al.[1)-4)].)

In general, the typology types are known as the Magneli phase, which is observed in the Ti-O system, the Aurivillius phase, well known by the general formula: $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$ for Bi-based high-temperature superconducting oxides, and the Ruddlesden-Popper phase with perovskite framework such as $SrO(SrRuO_3)_n$. The origin of these 3 crystal phases is briefly introduced below.

- Magneli phase:
  Transition metal oxides such as Ti, V, Mo, and W include a group of compounds that follow the general formula Ti_nO_{2n-1}, V_nO_{2n-1}, $Ti_{n-2}Cr_2O_{2n-1}$, Mo_nO_{3n-1}, W_nO_{3n-1} (n = an integer) exist in this phase. The crystal structure of this group of compounds has been intensively studied by Arne Magneli et al. in Sweden and is called the Magneli phase in their honor[5)].
- Aurivillius phase:
  Perovskite-derived crystal structure expressed by the general formula: $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ [where A is a large cation with a coordination number of 12 and B is a small cation with a coordination number of 6] exists in this phase. It is essentially a stack of alternating layers of $[Bi_2O_2]^{2+}$ and perovskite structures, studied in detail by Swedish chemist Bengt Aurivillius around 1949. Hence, this type of crystal structure is called the Aurivillius phase in his honor[6)-8)].

◆ Ruddlesden-Popper phase:

These are layered materials expressed by the general formula: $A_{n+1}B_nX_{3n+1}$ or $A_{n-1}A'_2B_nX_{3n+1}$. A and A' are alkali, alkaline earth, or rare earth metals, and B is a transition metal. Among the materials, Ruddlesden-Popper perovskites [$A_{n+1}B_nX_{3n+1}$], layered derivatives of a simple perovskite structure (ABX_3), are well known in the research field. The name originated from the research of S. N. Ruddlesden and P. Popper conducted in 1957 and 1958, and the academic term Ruddlesden-Popper phase has stuck since then[9), 10)].

References

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2) Noboru Kimizuka, Mitsumasa Isobe, Masaki Nakamura, Takahiko Mohri: "Syntheses and Crystallographic Data of the Homologous Compounds $InFeO_3(ZnO)_m$, (m = 1, 2, 3, 7, 11, 13, 15, and 19) and $Fe_2O_3(ZnO)_m$ (m = 8 and 9) in the In_2O_3-$ZnFe_2O_4$-ZnO System", J. So1id State Chem., 103, <2>, 394-402 (1993).
3) Masaki Nakamura, Noboru Kimizuka and Takahiko Mohri: "The Phase Relations in the In_2O_3-Ga_2ZnO_4-ZnO System at 1350°C", J. Solid State Chem., 93, <2>, 298-315 (1991).
4) Masaki Nakamura, Noboru Kimizuka, Takahiko Moori and Mitsumasa Isobe: "Synthesis and crystal structures of homologous phases $InFeO_3(ZnO)_m$ (m = natural number) and its isomorphous compounds", Kotai Butsuri, 28, <5>, 317-327 (1993). [in Japanese]
5) Arne Magneli: "Structures of the ReO_3-type with recurrent dislocations of atoms: 'homologous series' of molybdenum and tungsten oxides", Acta Crystallogr., 6, 495-500 (1953).
6) B. Aurivillius: "Mixed bismuth oxides with layer lattices: I. The structure type $CaNb_2Bi_2O_9$", Arkiv For. Kemi (1), 463-480 (1949).
7) B. Aurivillius: "Mixed bismuth oxides with layer lattices: II. Structure of $Bi_4Ti_3O_{12}$", Arkiv For. Kemi (1), 499-512 (1949).
8) B. Aurivillius: "Mixed bismuth oxides with layer lattices: III. Structure of $BaBi_4Ti_4O_{15}$", Arkiv For. Kemi (2), 519-527 (1950).
9) S. N. Ruddlesden and P. Popper: "New compounds of the K_2NiF_4 type", Acta Crystallogr., 10, <8>, 538-539 (1957).
10) S. N. Ruddlesden and P. Popper: "The compound $Sr_3Ti_2O_7$ and its structure", Acta Crystallogr., 11, <1>, 54-55 (1958).

using CO_2-H_2 mixture gas, precisely identifying the crystal structures of these materials. During this research period, in addition to $YFeO_3$ and $Y_3Fe_5O_{12}$, a new oxide with a hexagonal crystal structure, YFe_2O_4, was created, and the existence of a series of homologous oxides expressed as $FeO(RFeO_3)_m$ [R = Rare earth, Y] was discovered. In particular, YFe_2O_4 and $YbFe_2O_4$ discovered by Kimizuka et al., have become so famous that they are now referred to as the "$YbFe_2O_4$-type" crystal structure. Following the creation of $YbFe_2O_4$-type oxides by Kimizuka, the purpose of exploring the interesting magnetic physics of Fe spins in their unique two-dimensional configuration attracted the attention of prominent magnetic physics researchers around 1980, resulting in many papers, including those co-authored with Kimizuka[127)-134)].

Research on the new synthesis of materials containing iron (Fe) and their magnetic properties peaked around 1984 and continued until after 1990. However, as evident from Table 2.2, research concerning homologous multi-element oxides containing indium (In) is believed to have become the main theme of Kimizuka's work. Since most of the researched materials were homologous oxides that can be expressed with the general formula ($LnAO_3$) $nLnABO_4$ (n=0, 1, 2, /Ln=Y, Ho, Er, Tm, Yb, Lu, In, Sc, A=Fe, Ga, Al / B=Mg, Mn, Fe, Co, Cu, Zn, Cd), it can be inferred that Kimizuka's research shifted in a way that replaced Ln primarily with In.

Here, the author would like to unravel the sequence of research history focusing on the papers by Kimizuka et al. regarding homologous oxides containing In, especially the $InGaO_3(ZnO)_m$ homologous system containing Ga and $InGaZnO_4$, which corresponds to m=1 in the homologous system.

Before we delve into the study of metal multi-element oxides containing In, the paper[135)] listed in the left column of Table 2.2 is a report on the synthesis of layered oxides called $LnGaMO_4$ (where Ln = a lanthanide element, M = Mg, Mn, Co, Cu, Zn), most of which have lattice constants determined as $YbFe_2O_4$-type crystal structure. The compositions of interest are as follows.

- $TmGaZnO_4$: a = 0.34300(4) nm, c = 2.5066(5) nm
- $YbGaZnO_4$: a = 0.34153(5) nm, c = 2.5093(7) nm
- $LuGaZnO_4$: a = 0.34003(2) nm, c = 2.5253(3) nm

One of the earliest papers on In-based multi-element oxides[136)] discusses the crystal structures of $InGaCuO_4$ and $InGaCoO_4$, which have the same $YbFe_2O_4$-type crystal structure, and the following lattice constants.

- $InGaCuO_4$: a = 0.33497(2) nm, c = 2.4822(3) nm
- $InGaCoO_4$: a = 0.33091(2) nm, c = 2.5859(4) nm

A paper[137)] published in the following year, 1985, describes the important $InGaZnO_4$ composition as a crystalline phase. Its lattice constant is comparable to the description in the paper[125)] by O. Schmitz-DuMont et al. in 1965 mentioned above. However, in 1965, the concept of a new crystalline phase, the $YbFe_2O_4$-type crystal structure, did not yet exist. Thus, we can say that the paper by Kimizuka[137)] was the first

to establish the details of this crystal structure. This paper reported the lattice constants of the following crystalline phases classified as $YbFeO_4$-type crystal structure.

- $InGaZnO_4$: a = 0.32948(1) nm, c = 2.6071(1) nm
- $InGaMgO_4$: a = 0.33036(1) nm, c = 2.5805(1) nm
- $ScGaZnO_4$: a = 0.32593(1) nm, c = 2.5912(1) nm

Some papers have also reported the emission spectra of $InGaZnO_4$, $InGaMgO_4$, and $ScGaZnO_4$[138].

Kimizuka next considers the homologous phase of $InFeO_3(ZnO)_m$ (m=1 to 9) and analyzes the stacking of $InO_{1.5}$, $(FeZn)O_{2.5}$, and ZnO layers along the c-axis, as a result of which we see R3m symmetry when m is odd and $P6_3/mmc$ symmetry when m is even[139]. Furthermore, Kimizuka has reported substituting the Fe site with other elements as the same homologous oxides and confirmed that the c-axis lattice constant of $InGaO_3(ZnO)_m$ changes from m=1 to 7. In addition, compounds such as $InAlO_3(ZnO)_m$, $ScGaO_3(ZnO)_m$, etc., have been synthesized similarly, and the lattice constants at each m value have also been reported. The paper also mentions the observation of TEM lattice images of homologous $InGaO_3(ZnO)_5$ crystals at around the same time as Cannard's paper mentioned above[126]. In other words, this is a very important paper as it is considered to be the first to report TEM lattice images of homologous $InGaO_3(ZnO)_m$ crystals[139] and includes data on a series of homologous $InGaO_3(ZnO)_m$ crystal structures.

The paper in reference (140), which is a sequel to the previous paper[139], includes detailed studies of the solid solution ranges of 6 types of homologous $In_2O_3(ZnO)_m$-$Fe_2O_3(ZnO)_m$ (m = 1, 2, 3, 4, 5, 6), and the detailed investigation of the lattice constants of $In_2O_3(ZnO)_m$ and $Fe_2O_3(ZnO)_m$, respectively, with an m value up to 20. Therefore, the paper (140) is considered an important paper that approaches the true nature of the crystal structure chemistry of In-based homologous materials. Some research papers also report in detail on homologous $InGaO_3(MgO)_m$ (m = 1, 2), etc.[141].

Masaki Nakamura of the Kimizuka et al. group compiled the first detailed study of the crystal structure of homologous $InGaO_3(ZnO)_m$ up to m = 13 and the solid solution range between $In_2O_3(ZnO)_m$-$Ga_2O_3(ZnO)_m$[142]. The values of lattice constants for each m value of the $InGaO_3(ZnO)_m$ system are described in Table 2.3.

The In-Ga solid solution range from m = 1 to 13 was also studied in detail, and the results are presented in the following Table 2.4.

The solid solution range for $In_{1-x}Ga_{1+x}ZnO_4$ when m = 1 is $-0.33 \leq x \leq 0.08$, a very narrow solid solution range for a single phase compared to homologous systems with other m values. In the In-Ga solid solution range of any m value homologous system as well, data shows that the c-axis lattice constant takes a minimum value near the composition of $InGaO_3(ZnO)_m$ at x = 0 (i.e., In:Ga = 1:1), which the author assumes may be due to the unique crystal structure when x = 0 even in the solid solution region. This research paper also includes a deep crystallographic study regarding stacking in the c-axis direction as the m value of each In-Ga solid solution increases and the a-axis lattice constant approaches the axial length of bulk ZnO. Thus, this paper is extremely important as it analyzes the crystal structure chemistry of the homologous $InGaO_3(ZnO)_m$ system. Kimizuka et al. seem to have concentrated their research on whether the material itself can be thermodynamically stable. They published a detailed paper on solid solution formation between $In_2O_3(ZnO)_m$-$InAlO_3(ZnO)_m$[143], the same as the In-Ga system described above.

Kimizuka et al. also synthesized single-crystal homologous $In_2O_3(ZnO)_m$ (m = 3, 4, 5), $InGaO_3(ZnO)_3$, and $Ga_2O_3(ZnO)_m$ (m = 7, 8, 9, 16), and reported their lattice constant values[144]. For example, regarding the synthesis of single-crystal $InGaO_3(ZnO)_3$, small pieces of single crystals with a size of 0.02 x 0.1 x 0.1 cm^3 were obtained by heating at 1550°C for 5 days under excess ZnO and then annealing at 1350°C for a

Table 2.3 Lattice constants of homologous $InGaO_3(ZnO)_m$ crystal phases at each m value
(Prepared by the author from *J. Solid State Chem.*, 93, <2>, 298-315 (1991)[142].)

$InGaO_3(ZnO)_m$	Lattice Constants [nm]
$InGaO_3(ZnO)$	a=0.3296, c=2.602
$InGaO_3(ZnO)_2$	a=0.3292, c=2.251
$InGaO_3(ZnO)_3$	a=0.3288, c=4.156
$InGaO_3(ZnO)_4$	a=0.3284, c=3.289
$InGaO_3(ZnO)_5$	a=0.3280, c=5.713
$InGaO_3(ZnO)_6$	a=0.3277, c=4.299
$InGaO_3(ZnO)_7$	a=0.3276, c=7.279
$InGaO_3(ZnO)_9$	a=0.3270, c=8.828
$InGaO_3(ZnO)_{11}$	a=0.3266, c=10.38
$InGaO_3(ZnO)_{13}$	a=0.3258, c=11.92

Table 2.4 Solid solution range of homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ crystal phases
(Prepared by the author from *J. Solid State Chem.*, 93, <2>, 298-315 (1991)[142].)

$In_{1-x}Ga_{1+x}O_3(ZnO)_m$	Solubility Range in In-Ga
$In_{1-x}Ga_{1+x}O_3(ZnO)$	$-0.33 \leqq x \leqq 0.08$
$In_{1-x}Ga_{1+x}O_3(ZnO)_2$	$-0.68 \leqq x \leqq 0.32$
$In_{1-x}Ga_{1+x}O_3(ZnO)_3$	$-1.00 \leqq x \leqq 0.46$
$In_{1-x}Ga_{1+x}O_3(ZnO)_4$	$-1.00 \leqq x \leqq 0.54$
$In_{1-x}Ga_{1+x}O_3(ZnO)_5$	$-1.00 \leqq x \leqq 0.68 \sim 0.72$
$In_{1-x}Ga_{1+x}O_3(ZnO)_6$	$-1.00 \leqq x \leqq 0.68 \sim 0.79$
$In_{1-x}Ga_{1+x}O_3(ZnO)_7$	$-1.00 \leqq x \leqq 0.70 \sim 0.74$
$In_{1-x}Ga_{1+x}O_3(ZnO)_9$	$-1.00 \leqq x \leqq 0.56 \sim 0.72$
$In_{1-x}Ga_{1+x}O_3(ZnO)_{11}$	$-1.00 \leqq x \leqq 0.57 \sim 0.64$
$In_{1-x}Ga_{1+x}O_3(ZnO)_{13}$	$-1.00 \leqq x \leqq 0.49 \sim 0.75$

further 5 days.

Kimizuka et al. reported that the homologous material $InMO_3(ZnO)_m$ (M=In, Ga) has a modulation structure with high-resolution TEM observation[145]. This modulation structure is also mentioned in other papers[146), 147)] and seems to be a special structure often found in homologous systems.

From the above, the origin of the homologous $InGaO_3(ZnO)_5$ single crystal in field effect transistors published by Hosono et al. in Science[148)] in 2003 is thought to be closely related to the five papers [Refs = (137), (139), (142), (144), (145)] by Kimizuka et al. from the viewpoint of "substance". In that Science paper[148)], two of the five results of Kimizuka et al. are cited as representative references. In other words, it can be inferred that Hosono's group was fully aware of the history and background of such material technology.

In addition, I would like to note an interesting case related to this systematic survey. The reason is that Kimizuka has been conducting joint research with HOYA Corporation (hereafter referred to as HOYA) and has published three papers[149)-151)]. Masahiro Orita of HOYA and Hiromichi Ohta of HOYA co-authored three full papers and two papers, respectively, with Kimizuka, and both Orita and Ohta are participating together in the ERATO "HOSONO Transparent Electro-Active Materials Project" to be launched in the fall of 1999. However, it cannot be inferred from the titles of their joint research papers that they were directly targeting transparent conductive oxides. Rather, it is suspected that HOYA, a private company, wanted its own young researchers to absorb some of Kimizuka's advanced knowledge regarding homologous oxides. Eventually, both Orita and Ohta will become key researchers in the ERATO "HOSONO Project"; therefore, the existence of these coauthored papers is very interesting from the viewpoint of the relationships between the researchers in the future.

So far, research on homologous materials by the group at the National Institute for Research in Inorganic Materials led by Noboru Kimizuka has been surveyed. Next, I would like to introduce two interesting papers on homologous oxides by Massimo Nespolo, who was visiting and working at the same institute as Kimizuka. One is a study[152)] on $LuFeO_3(ZnO)_m$, while the other is research[153)] on $InGaZnO_4$ single crystals synthesized under high pressure. In particular, the latter involved growing single crystals under high pressures of 20 kbar and 50 kbar and performing respective structural analyses.

(3) Electrical and Optical Characteristics of Homologous Oxides studied by Toshihiro Moriga of Tokushima University

The group at the Institute for Research in Inorganic Materials (hereinafter referred to as NIRIM), led by Kimizuka et al., has conducted careful and sophisticated research on "substance" themselves, including thermodynamic stability, crystal lattice constants, crystal symmetry, solid solutions, and modulation structure through TEM observation, as described above, and they have published many significant papers. Based on the results of Kimizuka et al. above, it was Toshihiro Moriga et al. of Tokushima University who reported the electrical and optical evaluation of this homologous material, as described briefly in the section on multi-component oxides.

Moriga and Poeppelmeier co-authored three papers[94), 108), 109)], and while two papers[108), 109)], in which Moriga is credited as the first authors, are important, the third paper[109)] in which the electrical and optical properties of $InGaO_3(ZnO)_m$ were evaluated, is of particular importance. Before explaining the details of homologous $InGaO_3(ZnO)_m$, it is quite likely that the research on the $MgIn_2O_4$-$MgGa_2O_4$ solid solution system[154)] published by Moriga immediately before is the basis of this study, so we will briefly touch upon it. Moriga's paper is a study of the solid solution system $In_{2-x}Ga_xMgO_4$ and reports its existence in the following ranges[154)].

[I] $0 \leq x \leq 0.35$: In_2MgO_4-type crystalline phase

[II] $0.8 \leq x \leq 1.0$: $InGaMgO_4$-type layered structure

[III] $1.5 \leq x \leq 2.0$: Ga_2MgO_4-type crystal structure

The electrical conductivity decreases exponentially as the amount of Ga solid solution increases, and the evaluation of optical diffuse reflectance spectra shows that the optical band gap widens with the increase in the amount of Ga solid solution. The author believes that some of the research results from here are being applied to studying solid solution systems between $In_2O_3(ZnO)_m$ and $Ga_2O_3(ZnO)_m$.

The paper on the In-Zn-O homologous system $In_2O_3(ZnO)_m$ ($m = 3 \sim 11$) co-authored by Moriga and Poeppelmeier[108)] reports that conductivity exponentially increases as the number of ZnO layers (m value) sandwiched between In_2O_3 layers decreases, and that transmittance in the visible region increases (optical band gap widens) as the m value increases. We can thus see that this m value involves a trade-off between the factors of conductivity and transparency.

Next, the author presents very important results of a collaboration between Moriga and Poeppelmeier et al. on Ga-containing homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ solid solutions[109)]. In the report to determine the range of solid solution formation of $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ at each m value, it is judged that the results are almost similar to those of the previous study data[142)] by Kimizuka et al. In addition, several solid solution compositions of each m-value were extracted, and as-made samples and samples heat-treated in a reducing atmosphere were prepared. Their physical properties were then evaluated from electrical conductivity and diffuse reflectance spectra, respectively. The results are shown in Table 2.5.

Considering the solid solution range for each m value, it is reported that its c-axis lattice constant takes a minimum value when [In]:[Ga] = 1:1 and varies along Vegard's law for other [In]/[Ga] ratios. The results of this measurement reaffirm Kimizuka's research results[142)]. The author imagines that $InGaO_3(ZnO)_m$, which has a crystal structure of [In]:[Ga] = 1:1, may have a peculiar periodicity between the constituent elemental ions in its crystal structure.

On the other hand, when designing homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ solid solution as a transparent conducting oxide, if the policy of minimizing the number of ZnO

Table 2.5 Solid solution range of homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ crystal phases
(Prepared by the author from *J. Amer. Ceram. Soc.*, 82, <10>, 2705-2710 (1999)[109].)

(a) m-value of ZnO layers and solubility range in In-Ga in homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$

$In_{1-x}Ga_{1+x}O_3(ZnO)_m$	Solubility Range in In-Ga
$In_{1-x}Ga_{1+x}O_3(ZnO)$	$-0.34 \leqq x \leqq 0.06$
$In_{1-x}Ga_{1+x}O_3(ZnO)_2$	$-0.54 \leqq x \leqq 0.30$
$In_{1-x}Ga_{1+x}O_3(ZnO)_3$	$-1.00 \leqq x \leqq 0.42$

(b) Electrical conductivity in homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$

- ◆ Electrical conductivity increases as the number of ZnO layers decreases
- ◆ Electrical conductivity increases with increasing [In] concentration
- ◆ Reducing atmosphere treatment improves electrical conductivity

(c) Optical band gap in homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$

- ◆ Optical band gap increases as the number of ZnO layers decreases
- ◆ Optical band gap increases with increasing [Ga] concentration
- ◆ Reduction atmosphere treatment reduces optical band gap

layers (m value) for the same [In]/[Ga] ratio is adopted, heat treatment under a reducing atmosphere will improve electrical conductivity; however, the transparent wavelength range in the visible region is reduced. Increasing the [In] concentration to increase the electrical conductivity by adjusting the [In]/[Ga] ratio results in a trade-off problem in that the optical band gap is reduced. This trade-off problem is thought to be common to many transparent conducting oxides, not just this homologous system.

In any case, the most significant aspect of this paper[109] co-authored by Moriga and Poeppelmeier, is that it is the first evaluation of the physical properties of homologous $In_{1-x}Ga_{1+x}O_3(ZnO)_m$ solid solutions, especially their electrical and optical properties. From this background, it is considered to have important relevance from the viewpoint of material and physical property evaluation to a paper on field-effect transistors using $InGaO_3(ZnO)_5$ homologous crystals published in *Science* in 2003[148].

(4) Suggestion of the Possibility of Amorphous Phases by the Joint Research of Toshihiro Moriga and Kikuo Tominaga and Subsequent Developments

A look at the change in research papers by Moriga et al. since 2000 shows that they revisited and re-examined the basic compositions of ZnO and In_2O_3-ZnO oxide thin films. By about 2005, the following list of papers had been published. [Numbers in parentheses ( ) are reference numbers]

- ◆ Report on ZnO:Al-ZnO system: (155), (156), (157)
- ◆ Report on Zn-In-O system: (158), (159), (160), (161)
- ◆ Report on amorphous ZnO-In_2O_3 system: (162), (163), (164), (165), (166), (167), (168), (169), (170)
- ◆ Report on ZnO-SnO_2 [homologous crystal + amorphous] system: (171), (172)

During this period, a joint research team consisting of Toshihiro Moriga of the Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, and Kikuo Tominaga of the Department of Electrical and Electronic Engineering, Faculty of Engineering, The University of Tokushima, demonstrated the existence of amorphous films in the In-Zn system that can be sufficiently used as transparent conductive films, and also discovered that the surface smoothness of an amorphous film can be significantly improved by annealing heat treatment while maintaining its structure[168]. Since most research papers on transparent conducting oxide thin films to date have focused on the crystalline phases, such as homologous structures, the fact that Moriga et al. have clearly demonstrated the direction of transparent conducting thin films in an amorphous state is considered to be unique from the materials design perspective.

Specifically, Moriga et al. discovered that when ZnO-In_2O_3-based transparent conductive films were synthesized at a substrate temperature of 150°C using a DC sputtering device with opposing targets, amorphous phases were formed in a wide range of compositions. In particular, amorphous thin films on the In-rich side exhibited a minimum resistivity of 2.3×10^{-4} Ω·cm[162]. The composition ratio of the amorphous phase that gives low resistivity, Zn/(Zn+In), is in the range of 0.2 to 0.4., and Moriga et al. also found that the composition ratio range can be increased to 0.3 to 0.6 while maintaining this low resistivity by adding 3% by weight of Al_2O_3[166), 167]. In addition, it was confirmed that the optical band gap also widens slightly. From these facts, it is considered that they discovered there might be room to adjust the Zn/In ratio to a certain extent while maintaining the low-resistance condition in an amorphous state. Furthermore, annealing the amorphous Zn-In-O film would significantly improve the smoothness of the thin film surface while maintaining its conductivity[165), 167), 168]. Since these In-Zn-O thin films are mostly used as transparent electrodes for devices, securing the technology to fabricate these highly planar, low-resistance thin films is considered a very important research achievement from an industry perspective.

As mentioned above, Moriga et al. felt that the Zn-In-O thin film investigated between 2000 and 2004 was sufficiently responsive as a transparent conducting film even in an amorphous state, and it is imagined that they developed their research as the "Third-Generation Transparent Conducting Amorphous Oxide Thin Films"[168]. To the best of the author's knowledge, only one design guideline in the past has allowed a final product in the state of amorphous thin film, such as this Moriga. The only case in this point was a lecture, "Working hypothesis to explore novel wide band gap electrically conducting amorphous oxides and amorphous oxides and examples", by Hideo Hosono at "the Sixteenth International Conference on Amorphous Semiconductors - Science and Technology (16th-ICAS)" held in Kobe in September 1995. (The contents are published in *the Journal of Non-Crystalline Solids*, 198-200, <1>, 165-169 (1996)). In advocating the common amorphous line, Moriga must have also been standing on the same stage, following Hosono's back. Hosono has

been presenting the original approach of amorphous transparent oxide semiconductors (transparent conductive oxides) in his solitary efforts at many academic conferences since 1995. The history of materials exploration is truly interesting when the author imagines that Moriga also thought there was no problem with the amorphous route rather than the crystalline route and that he may have been following Hosono's research through his own experiments. Moriga must also have had an excellent sense of how to arrive at the idea that even an amorphous state could be a thing without being bound by preconceived notions, like Hosono.

As a supplementary note, several years after Hosono's *Nature* publication, Moriga and Tominaga's team showed that the incorporation of Ga in In-Zn-O enabled amorphization over a wider composition range and improved transmittance in the blue wavelength region[173), 174)]. In addition, they have published a lot of data supporting Hosono's IGZO-TFT technology, including confirmation that the optical band gap can be widened from 3.91 eV to 4.06 eV by increasing the Ga content[175), 176)].

Since 2008, a group at the National Institute for Materials Science (NIMS: formerly the National Institute for Research in Inorganic Materials), led by Yuichi Michiue et al. has been researching homologous $Ga_2O_3(ZnO)_m$[177)-180)], while an international team led by the University of Bonn in Germany has been researching the In-Ga-Zn-O system[181), 182)], and several papers having been published on homologous oxides[183)-187)]. Among them, a joint research by Kyushu University and Idemitsu Kosan Co., Ltd. reported that the In-Zn-O system undergoes a superconducting transition at extremely low (cryogenic) temperatures, which is a very interesting phenomenon from the perspective of pure condensed matter physics[187)].

Until now, this chapter has discussed the background of research and development of homologous transparent conducting oxides from the author's point of view, beginning with the history of ITO, followed by multi-element oxides such as In-Zn-O and In-Zn-Sn-O, and homologous oxides such as $InGaO_3(ZnO)_m$. The research and development of transistors using oxide semiconductors, which will be discussed later, is being conducted alongside materials research on transparent conducting oxides, thus serving as a reminder of the importance of continuous and steady basic research on material technology. On the other hand, some descriptions regarding transparent conductive materials may not be accurate due to the author's insufficient study, and he thus asks for your understanding. Because of their actual use, many excellent documented publications are available in the field of transparent conductive materials. For comprehensive information on the chemistry and physics (including electronic and optical properties) of crystal structures, chemistry, and thin film deposition processes, please refer to the reference books written by experts[188)-199)].

Column: A Short History of Metal-Semiconductor Junction Potential Barriers (Contact Resistance) and Rectifiers

The study of transparent electrodes requires certain knowledge. That is the existence of a potential barrier between materials that are in contact with each other. Since transparent electrodes are often directly bonded to the wiring metal on one side and a liquid crystal or organic electroluminescent material on the other, the contact resistance between the electrode and other materials should be reduced as much as possible to achieve a so-called ohmic junction. In this context, the author will briefly touch upon the history of the phenomenon of electric rectification and subsequent potential barriers in metal-semiconductor junctions.

The phenomenon of electric rectification was discovered more than a hundred years ago in 1874 by German physicist Karl Ferdinand Braun[1)]. The rectification effect was first discovered using an arrangement in which a metal needle is thrust into a metal sulfide and measuring the change in resistance by changing the current direction. Braun's achievement is extremely famous today as the invention of the cathode ray tube in 1897[2)].

In addition, Cu-Cu_2O-based rectifiers also have a long history, dating back to the research of Lars Olai Grondahl around 1930[3)-6)]. Also during this period (1930), Gennosuke Hara of the Ryojun College of Engineering, a Japanese university at that time, published a detailed study concerning the rectification effect, which is very interesting even in terms of understanding the high level of knowledge at the time[7)]. Further details on Cu-Cu_2O-based rectifiers can be found in reports by Maruyama et al.[8)] and Sawaji[9)]. The historical evolution of practical rectifiers using various materials such as Se, Cu_2O, Ge, and Si are described in detail in the commentary by Tatsusaburo Masada of Origin Electric Co., Ltd.[10)]. Regarding the application and industrialization of rectifiers, Cu_2O-based rectifiers (invented in the U.S.) were developed around the 1920s, followed by Se-based rectifiers in Germany in 1928. The development of rectifiers in Japan took place after the war. Ge-based rectifiers were industrialized in the U.S. in 1952, and following the invention of the transistor in the 1950s, Si-based rectifiers replaced Ge-based rectifiers. In Japan, Masami Tomono of Hitachi, Ltd. is widely known for his research on the rectification effect of selenium[11), 12)].

In 1939, Sir Nevill Francis Mott[13)] and Walter Hans Schottky[14)] proposed a theory on the rectification mechanism of

cuprous oxide (Cu_2O) and selenium (Se), and the concept of potential barrier at the interface between a metal and semiconductor was introduced. The electron potential energy barrier formed at the metal-semiconductor junction is widely known today as the Schottky barrier, which enables the junction device to have rectification properties and become a diode. This barrier was useful in understanding the mechanism of rectifier properties at the time. In the 1950s and 1960s, selenium rectifiers were widely used for TV power supply, and in addition to selenium, cadmium compounds were often used in element junctions. Most have now been replaced by devices such as silicon diodes. The theory regarding metal-semiconductor junction potential barriers was revised and developed by Hans Albrecht Bethe and published in the Radiation Laboratory Report[15] of the Massachusetts Institute of Technology (MIT) on November 23, 1942.

When designing transparent electrodes, it is necessary to suppress the barrier caused by the metal-semiconductor junction and achieve an ohmic junction as much as possible. Therefore, it is necessary to design materials for both sides by combining the work function Φ_M of the metal, which in this discussion means a transparent conducting oxide that serves as a transparent electrode, the electron affinity χ_S of the semiconductor when the material to be junctioned is a semiconductor, and the energy band gap E_g, such that the following conditions for ohmic junction are satisfied.

< i > When the other semiconductor is n-type (carriers are electrons): $\Phi_M < \chi_S$

<ii> When the other semiconductor is p-type (carriers are holes): $\Phi_M > \chi_S + E_g$

Therefore, when developing transparent conducting oxides for use in transparent electrodes, it is important to improve transmittance while improving conductivity and carrier density and also to give full consideration to the physical relationship between the work function of the material with the other material (semiconductor or metal) to be junctioned.

Research on alloy materials for junctions that consider the ohmic wiring to ITO films of transparent electrodes exactly aligns with this perspective. According to a specific example cited in a report by the Kobe Steel Group, adjusting the AlOx layer that forms at the junction interface is key. An alloy composition of Al-2at%Ni-0.35%La, in which aluminum (Al) is mixed with a small amount of nickel (Ni) and a trace amount of lanthanum (La), is reported to provide highly linear ohmic properties[16), 17)]. The search for materials for such junctions is an important issue for the entire TFT device.

Hosono's group has also published a research paper exploring metal electrodes suitable for amorphous IGZO[18)]. Around the same time, J. F. Wager of Oregon State University conducted a detailed study on the ohmic and Schottky properties in electrodes[19)]. In the same year, the Fan Ren et al. group at the University of Florida[20), 21)] published a comprehensive report on reducing contact resistance by measuring the contact resistance of an electrode (Ti/Au) with n-type amorphous IZO thin films using the Circular-TLM method and band offset, etc. A Korean research group[22)] has announced a unique device that intentionally creates a Schottky barrier during transistor operation. In addition, a group from Northwestern University and Argonne National Laboratory in the U.S.[23)] used the Kelvin probe method to investigate the work functions of various conducting oxides in both amorphous and crystalline states, which is very important. It is interesting to note that this paper also investigates work functions after ozone treatment. A Chinese research team has also conducted research[24)] on the contact resistance between amorphous IGZO and electrodes.

Naturally, companies in Japan and abroad must have already developed suitable materials for such contact parts, often treated as a private area where no patent applications were filed, and technologies were kept secret when analysis technology was not as advanced. However, now that it is possible to conduct composition and depth profile analyses at the nanoscale, the material technology for junction parts, which is essential for device configuration, is increasingly being disclosed to ensure a channel for in-house technology. Concerning the commercialization of IGZO-based oxide semiconductor transistors, the R&D group of Kobe Steel has been researching and developing wiring materials, cap layer materials, etc. It has identified important points and interesting material systems in the fabrication of transistor devices[25)].

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2.3 Examples of Transparent Conductive Oxides Attracting Attention from Applications in Other Fields

2.3.1 Thermoelectric Conversion Materials

Thermoelectric conversion materials are special materials required for a large thermoelectric force, high electrical conductivity, and low thermal conductivity. On the other hand, the Wiedemann-Frantz law states that the ratio of the thermal conductivity κ to the electrical conductivity σ of a material (mainly metals) is equal to the product of the absolute temperature T and a constant L that is independent of the type of material, expressed by the following formula.

$(\kappa/\sigma) = LT$ (L: constant in Lorentz number)

Since the ratio of the thermal conductivity κ to the electrical conductivity σ of metal is constant because of these restrictions on the material, a dilemma is presented when designing high-performance thermoelectric conversion materials, namely the search for materials with lower thermal conductivity while maintaining high electrical conductivity, which is generally very difficult.

Under such circumstances, some researchers in the mid-1990s gained interest in homologous oxides as a new approach to exploring new thermoelectric conversion materials. One of them was Kunihito Koumoto[200)-203)], a professor at Nagoya University. Various research approaches are known for the design of thermoelectric conversion materials. One is a search method using layered crystal materials from the idea of using anisotropy in the c-axis direction and the a-b plane. A research group led by Kunihito Koumoto et al. was the first to experiment with this search method and publish their results[204)]. They chose $In_2O_3(ZnO)_m$, a homologous oxide that was expected to have anisotropy, and this is the first evaluation report on its thermoelectric force[204)]. When the Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) of 3 samples (m = 5, 7, 9), obtained by sintering a mixture of In_2O_3 and ZnO in the air at a high temperature of 1550°C for 2 hours, were measured in the temperature range of 500 K ~ 1100 K, it was found that the larger the m value, the larger the numerical value of each item. In the case of $In_2O_3(ZnO)_9$, where m = 9, the performance index at a high temperature of 1000 K remained about 0.1. The performance index is expressed as ZT, where $Z = S^2\sigma/\kappa$ and $ZT > 1$ is generally considered the goal in material search. The first author of this paper is Hiromichi Ohta, who would later participate in the launch of Hosono's ERATO project.

Next, Koumoto et al.'s group fabricated homologous

$In_2O_3(ZnO)_5$-based thin film using the sputtering deposition method and performed its evaluation[205]. Their paper is considered to be the first to discuss the thermoelectric properties of homologous oxide thin films. The microstructure, the temperature dependence of the Seebeck coefficient and electrical conductivity in each preferred oriented film were measured. Although the electrical conductivity in the direction perpendicular to the c-axis (in the a-b plane) was several times higher than in the c-axis direction, anisotropy did not significantly improve thermoelectric properties. The first author, Hidenori Hiramatsu, also evaluated the optical properties and electrical conductivity, reconfirming its potential as a transparent conducting oxide[206].

At the same time, members of the Koumoto laboratory modified the homologous system by substituting the In site with Y. They reported that substituting with 3% Y had the greatest effect on the thermoelectric performance index, with the performance index exceeding 0.1 at 1000 K[207), 208]. Koumoto et al., in collaboration with Toshihiko Tani et al. of Toyota Central R&D Labs., Inc., reported adapting the reactive templated grain growth method[209], previously developed by Tani et al., to homologous $In_2O_3(ZnO)_5$[210), 211]. By 2004, Koumoto and Tani et al. also reported several improvements to HIP sintered, single-crystal, and Ca-substituted materials[212)-215].

The dozen or so papers introduced here are all material search routes that take the anisotropy of the crystal structure as a new approach in hopes of breaking away from the proportional correlation between σ and κ. The reason the author chose to discuss thermoelectric conversion materials in this section is because they are a homologous phase similar to $InGaO_3(ZnO)_m$, which is used for the channel layer of the transistor published by Hosono in Science paper in 2003 (however, it is not a system containing Ga) and the similarity in focusing on electronic properties, and also because Hiromichi Ohta, who was the first author of the first paper published in 2003[204], joined Hosono's ERATO project a few years later. From this perspective, it is believed that the 2 papers[204), 205] introduced here occupy an important place in Hosono's materials genealogy, leading to the paper in *Science*.

In addition, the author wants to add some recent information regarding thermoelectric conversion materials. The group of Prof. Hiromichi Ohta of the Research Institute for Electronic Science (RIES) at Hokkaido University utilized the fact that $InGaO_3(ZnO)_m$ single-crystal thin films fabricated using the reactive solid-phase epitaxial growth method, which Ohta himself had developed in the Hosono Transparent ElectroActive Materials, Exploratory Research for Advanced Technology (ERATO Project), form a natural superlattice structure, and discovered that thermal conductivity in the direction perpendicular to the superlattice direction is lower than that of polycrystals[216]. These research results are not just the usual concept of anisotropic heat conduction in the c-axis direction and the c-plane due to anisotropy but demonstrate that thermal conduction of single crystals in the c-plane can be reduced even more significantly than in polycrystals, which were originally considered to have lower thermal conduction than single crystals providing a significant hint to the design of low thermal conducting materials or thermal management technology. Prof. Ohta of Hokkaido University is an experienced researcher, having worked at the Kunihito Koumoto laboratory, HOYA, and JST's ERATO Hosono project, and his significant development as a graduate member of Hosono's project can be seen. The author will introduce one more report here. Takayoshi Katase et al., associate professor at the Laboratory for Materials and Structures of Tokyo Institute of Technology and part of Toshio Kamiya's group, who will succeed Hosono, used $LaTiO_3$, a Mott insulator to make it metallic using lattice distortion (compressive stress) caused during epitaxial film deposition, and by changing the conduction carrier from p-type to n-type, breaking the conventional trade-off relationship between S and σ and identifying a region of proportionality, clearly showing a route for material search that significantly improves the performance index[217]. This search process is a highly scientific material design route discovered due to a deep understanding and exploration of the nature of solid-state physics. These discoveries by the Hiromichi Ohta group at Hokkaido University and the Katase-Kamiya group at Tokyo Institute of Technology are significant because they attempt to delve into the nature of materials science and lay the foundation for material search.

Today, several commentaries[218)-230] and reviews[231)-236] have been published in international journals concerning thermoelectric conversion materials using oxides, and the author sincerely hopes that the above challenging efforts will spread to many young researchers and serve as a stepping stone toward solving thermal management and energy issues around the world.

2.3.2 Phase Change Optical Memory Materials

Phase change optical memory materials are those generally utilizing the phase change between crystalline and amorphous. The common recording method proceeds as follows. First, an amorphous film of the desired composition is prepared by sputtering, etc., The amorphous film is initialized by heat-treating it to crystallize the entire film. This step is followed by irradiating with a laser beam to raise the high temperature above the melting point of the thin film material (e.g., 600°C) and rapid quenching, resulting in only the irradiated section becoming amorphous (having low reflectivity). During erasure, the thin film is heated to a temperature above the crystallization temperature (e.g., 400°C) and then slowly cooled to a crystalline state (having high reflectivity). Chalcogenide materials such as GeSbTe, published by a research group at Matsushita Electric Industrial Co., Ltd. (now Panasonic Holdings Corporation) in 1987, are well-known phase change optical memory materials[237)-239].

A joint research group led by Prof. Masanori Okuyama of Osaka Prefecture University and Prof. Tatsuhiko Matsushita of Osaka Sangyo University had also been conducting research on chalcogenide-based optical recording materials

since the early 1990s[240]. Thereafter, they switched to a material system containing In and continued their research, intending to use it as transparent conductive thin films. Since around 1996, they have published many research reports[241)-255)], also mentioned in this systematic survey as relevant information.

At the time, a certain amount of optical absorption in the blue wavelength band was necessary since recording at blue wavelengths was attracting attention from the perspective of high-density optical recording materials, and widening the band gap was one of the important issues in designing optical recording materials. Since the material design of transparent conducting oxides for use in transparent electrodes also shared these same issues, it is considered that the joint research group conducted their research with an eye on the development of both phase change optical recording materials and transparent conducting oxides.

In their series of papers such as this one, two papers[245), 251)] concern the In-Ga-Zn-O system, the same compositional system as Hosono et al. In the first paper by Tatsuhiko Matsushita et al.[245)], In-Ga-Zn oxide thin films were fabricated at room temperature through magnetron sputtering. Since the as-made film was a thin film of Zn metal mixed with some ZnO phase having a band gap of 3.6 eV from its absorption edge after annealing at 350°C, the paper points out the possibility that In-Ga-Zn oxide thin-film was formed. The Matsushita et al. group did not discover this material system on their own, since they cite 3 papers used as reference material: New ultraviolet-transport electroconductive oxide, $ZnGa_2O_4$ spinel by Hiroshi Kawazoe et al. at Tokyo Institute of Technology[256)], A New transparent conducting oxide, $InGaZnO_4$ by Masahiro Orita et al. of HOYA[257)], and information on $Zn_2In_2O_5$ transparent conducting film by Minami et al.[258)] of Kanazawa Institute of Technology. Rather, it is assumed that the group was promptly studying the latest technical information on oxide semiconductors and transparent conductive films and investigating the potential application in their specialty in phase change optical recording materials. The optical recording properties of In-Ga-Zn-oxide thin films enable recording to be sufficiently performed even under half the optical power conditions of recording for Ge-Sb-Te films, leading to the conclusion that In-Ga-Zn-oxide thin films are a promising candidate for phase change optical recording materials. In the second paper[251)], though the composition of the thin film material fabricated in the experiment was considerably different from the composition ratio of In:Ga:Zn = 1:1:1, generally Ga component was lower and In component was higher. Therefore, it is believed that the composition range was also significantly different from that of $InGaZnO_4$-based materials for transparent conductive films and transistors.

In a book titled "Technology and Materials for Future Optical Memories"[259)] supervised by Masahiro Okuda and published in January 2004, Chapter 3, Section 5 titled "Blue laser-compatible oxide-based write-once optical recording films", written by Tatsuhiko Matsushita, a professor of Osaka Sangyo University, gives a detailed description of Zn-In-Ga-O thin films. In addition to the paper by Cava et al. of Bell Laboratories[32)], two co-authored papers by Moriga of Tokushima University and Poeppelmeier of Northwestern University[108), 109)] are cited as references, suggesting that the findings on transparent conducting oxides had also become a subject of interest in the field of phase change optical recording materials.

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250) Takanori Aoki, Akio Suzuki, Tatsuhiko Matsushita and Masahiro Okuda: "Metal Indium and Gallium Oxide Optical Recording Films Prepared by Radio-Frequency Magnetron Sputtering", J. Vac. Soc. Jpn., 43, <3>, 292-295 (2000). [in Japanese]
251) Takanori Aoki, Akio Suzuki, Tatsuhiko Matsushita and Masahiro Okuda: "High-Density Optical Recording Disk for Blue Laser Diode using Films Composed of Metal and Oxide", J. Vac. Soc. Jpn., 44, <3>, 244-247 (2001). [in Japanese]
252) Akio Suzuki, Tatsuhiko Matsushita, Takanori Aoki, Yoshitaka Yoneyama and Masahiro Okuda: "Pulsed Laser Deposition of Transparent Conducting Indium Tin Oxide Films in Magnetic Field Perpendicular to Plume", Jpn. J. Appl. Phys., 40, Part 2, <4B>, L401-L403 (2001).
253) Akio Suzuki, Akihito Mori, Jun Sakamoto, Yoshiyuki Tani, Takanori Aoki, Tatsuhiko Matsushita and Masahiro Okuda: "Transparent Conducting Indium Tin Oxide Films Prepared by Pulsed Laser Deposition Using High Power ArF Excimer Laser", J. Vac. Soc. Jpn., 45, <3>, 243-246 (2002). [in Japanese]
254) Takanori Aoki, Shin Akiduki, Akio Suzuki, Tatsuhiko Matsushita and Masahiro Okuda: "Improvement of Characteristics on Optical Disk at the Wavelength of Blue Laser", J. Vac. Soc. Jpn., 45, <3>, 247-250 (2002). [in Japanese]
255) Takanori Aoki, Akio Suzuki, Tatsuhiko Matsushita, Kazutoshi Shigeta and Masahiro Okuda: "Optical Recording Films with Laminated Multilayer Structure ZnO/In_2O_3 Prepared by Pulsed Laser Deposition Method", The transactions of the Institute of Electrical Engineers of Japan. C, 123, <11>, 1925-1929 (2003). [in Japanese]
256) Takahisa Omata, Naoyuki Ueda, Kazushige Ueda and Hiroshi Kawazoe: "New ultraviolet-transport electroconductive oxide, $ZnGa_2O_4$ spinel", Appl. Phys. Lett. 64, 1077-1078 (1994).
257) M. Orita, H. Sakai, M. Takeuchi, Y. Yamaguchi, T. Fujimoto and I. Kojima: "A New Transparent Conductive Oxide, $InGaZnO_4$", Trans. Mater. Res. Soc. Japan, 20, 573-576 (1996).
258) Tadatsugu Minami, Hideo Sonohara, Toshikazu Kakumu and Shinzo Takata: "Highly Transparent and Conductive $Zn_2In_2O_5$ Thin Films Prepared by RF Magnetron Sputtering", Jpn. J. Appl. Phys., 34, <8A>, L971-L974 (1995).
259) Masahiro Okuda (Supervised): "Technology and Materials for Future Optical Memories", CMC Publishing Co., Ltd. (January 31, 2004). In particular, Chapter 3, Section 5, pp.172-202, "Blue laser-compatible oxide-based write-once optical recording films" by Tatsuhiko Matsushita (Author) is interesting. [in Japanese]

3 Hosono's Working Hypothesis and its Theoretical Construction for the Creation of Novel Oxide Semiconductors

3.1 Creation of Wide-Gap Oxide Semiconductor Groups at the Dawn of Materials Design

3.1.1 A Huge Number of Papers on Novel Functional Oxides Created by Hosono and Kawazoe's Laboratory

One of the two valuable papers by Hideo Hosono's group was published in *Science* [*Science*, 300, 1269-1272 (2003)], which reported on the creation of high-performance transparent field-effect transistors that operate at a high mobility level approaching that of polysilicon using an oxide semiconductor crystal, $InGaO_3(ZnO)_5$ in the active layer, and another in *Nature* [*Nature*, 432, 488-492 (2004)], which reported on the creation of thin-film transistors using amorphous oxide semiconductor a-$InGaZnO_4$ as the active layer, with an electron mobility 10 times higher than that of conventional amorphous silicon, and which can be processed at low temperature. If we consider the history of accumulation of technology that led to these excellent papers, it is found that a major foundation had been laid by a large number of significant research outcomes published by Kawazoe-Hosono's laboratory, which were inherited by Honorary Professor Hideo Hosono, then assistant professor, from Professor Emeritus Hiroshi Kawazoe, then professor, at Tokyo Institute of Technology (hereinafter abbreviated as Tokyo Tech) from 1992 to around 2004.

Here, in addition to the above-mentioned research period, the papers of Hosono and Kawazoe on specific material creation by their original material exploration methods for wide-gap oxide semiconductors[1)-113)], including those in the years after 2004 that seem directly related to the *Science* paper in 2003 and the *Nature* paper in 2004, are summarized and listed in Table 3.1.

This list is presented in an easy-to-understand manner, with divisions based on the author's perspective, such as individual oxide materials that have been the subject of discovery or conductive mechanisms, heteroepitaxial growth technology, p-n junction technology, homologous crystal oxide-related technology, related to amorphous $InGaZnO_4$ (a-IGZO) materials, and proposals, general remarks, and reviews. Among these papers exceeding 100, the noteworthy research results from the viewpoint of the author are the 2 papers related to the design and creation of p-type oxides[25), 96)], the proposed working hypothesis for the material design guideline for transparent amorphous oxide semiconductors[91)] (including the creation of various oxide materials that was underway at the same time), the achievement of p-n junction diode characteristics by all amorphous oxides[62)], and the reactive solid-phase epitaxy method, which played an important role in the realization of field-effect transistors using single crystals[66)-68), 73), 74), 76), 104)].

3.1.2 Two Wheels of a Car, Hiroshi Kawazoe and Hideo Hosono

The period from the 1990s to 2004 laid the foundation for Hosono's career as a researcher and is imagined to be the most combustive and turbulent period. Looking back at the published career of Hosono[114), 115)], he was appointed assistant professor at the Department of Materials Science and Engineering, Nagoya Institute of Technology in March 1990. Later, after being called out by Prof. Hiroshi Kawazoe of Tokyo Tech, he joined the Research Laboratory of Engineering Materials at Tokyo Tech in July 1993. In April 1995, he was transferred to the Institute for Molecular Science, Okazaki National Research Institute (hereinafter abbreviated as the Institute of Molecular Science) as an assistant professor (held a concurrent post at Tokyo Tech) and again returned as assistant professor to Materials and Structures Laboratory at Tokyo Tech in April 1997, and was appointed professor at Materials and Structures Laboratory at Tokyo Tech. Meanwhile, Kawazoe, Hosono's superior, was appointed professor at Tokyo Tech in 1990; three years later, he took a concurrent post of professor at the Institute of Molecular Science. That was when Kawazoe precisely invited Hosono to Tokyo Tech. Two years later, Kawazoe returned to Tokyo Tech from the Institute of Molecular Science, where he held a concurrent post, this is when Hosono is considered to have been transferred to the Institute of Molecular Science. (During this period, Hosono also held a concurrent post at Tokyo Tech) Two years before Kawazoe retired in 1999, he brought Hosono back to Tokyo Tech to succeed him. Upon his retirement, Kawazoe was invited by HOYA Corporation (hereinafter referred to as HOYA) and was appointed as the head of their newly established Special Laboratory to facilitate research and development within the company[116)]. Meanwhile, after Kawazoe's retirement, Hosono was appointed professor at Tokyo Tech through an open selection process.

Thus, Kawazoe and Hosono must have been like two wheels of a cart, overcoming the stormy seas of nearly a decade of research upheaval with their outstanding communication, despite being regarded as heretics. "I do not have a specific mentor. The reason is that I learned basic science through books and learned the style of research from original research papers. In fact, even after entering my research life, I have followed my own path, not joining the mainstream world from time to time". The series of columns by Hiroshi Kawazoe that appeared in *NEW GLASS* magazine, beginning with the above paragraph, are very interesting indeed[117)-121)]. In his column[118)], Kawazoe states the paper[122)] in which the important conclusion that structural strain in glass is distributed according to the chemical bond strength of each component is visually demonstrat-

Table 3.1 A list of specific research results on wide-gap oxide semiconductors from Hosono and Kawazoe's original and unique material exploration

◆ **$MgIn_2O_4$**
Appl. Phys. Lett., 61, 1954-1955 (1992).
Jpn. J. Appl. Phys., 32, L1260-L1262 (1993).
J. Appl.Phys., 76, 7935-7941 (1994).
Nucl. Instrum. Methods Phys. Res., Sect. B, 106, <1–4>, 517-521 (1995).
J. Non-Cryst. Sol., 182, 109-118 (1995).
Solid State Phenomena, 51-52, 317-322 (1996).
J. Ceram. Soc. Japan, 105, <3>, 275-277 (1997).
Mater. Sci. Eng.: B, 54, <1–2>, 51-54 (1998).
MRS Symp. Proc., 623, 297-302 (2000).
J. Appl. Phys., 91, 2112-2117 (2002).
Phil. Mag. B, 82, <10>, 1155-1162 (2002).

◆ **$CdGa_2O_4$**
Appl. Phys. Lett., 62, 499-500 (1993).

◆ **$ZnGa_2O_4$**
Appl. Phys. Lett., 64, 1077-1078 (1994).

◆ **$CdSb_2O_6$, $Cd_2Sb_2O_7$**
Appl. Phys. Lett., 63, 3335-3337 (1993).
Appl. Phys. Lett., 65, 406-408 (1994).
Jpn. J. Appl. Phys., 33, L238-L240 (1994).

◆ **a-Cd_2GeO_4**
Appl. Phys. Lett., 67, 2663-2665 (1995).
J. Am. Ceram. Soc., 80, <1>, 22-26 (1997).
J. Non-Cryst. Sol., 274, 313-318 (2000).
Phys. Rev. B 66, 035203 (2002).

◆ **a-$AgSbO_3$**
J. Ceram. Soc. Japan, 103, <5>, 455-459 (1995).
Jpn. J. Appl. Phys., 34, <3A>, L281-L285 (1995).
Solid State Commun., 95, <6>, 399-403 (1995).

◆ **a-Cd_2PbO_4**
Appl. Phys. Lett., 68, 661-663 (1996).

◆ **$CuAlO_2$**
Nature, 389, 939–942 (1997).
J. Appl. Phys., 88, 4159-4163 (2000).

◆ **$SrCu_2O_2$**
Appl. Phys. Lett., 73, 220-222 (1998).
J. Appl. Phys., 91, 3074-3078 (2002).

◆ **$AgInO_2$**
Appl. Phys. Lett., 72, 1036-1038 (1998).
J. Appl. Phys., 88, 3067-3069 (2000).

◆ **β-Ga_2O_3**
Appl. Phys. Lett., 70, 3561-3563 (1997).
Appl. Phys. Lett., 71, 933-935 (1997).
Appl. Phys. Lett., 77, 4166-4168 (2000).
MRS Symp. Proc., 666, F2.9.1-F2.9.6 (2000).
Thin Solid Films, 411, <1>, 134-139 (2002).

◆ **$CuInO_2$**
Appl. Phys. Lett., 78, 1583-1585 (2001).
Solid State Commun., 121, <1>, 15-17 (2001).
MRS Symp. Proc., 666, F3.14.1-F3.14.6 (2001).

◆ **$CuGaO_2$**
J. Appl. Phys., 89, 1790-1793 (2001).

◆ **$ZnRh_2O_4$**
Appl. Phys. Lett., 80, 1207-1209 (2002).
MRS Symp. Proc., 747, V2.2.1-V2.2.6 (2002).
Adv. Func. Mater., 15, <6>, 968-974 (2005).

◆ **Li-doped NiO**
J. Mater. Res., 19, 913–920 (2004).

◆ **ZnO**
Phys. Rev. B, 70, 125415 (2004).

◆ **Epitaxial-In_2O_3 ZnO, ITO Films on YSZ**
MRS Symp. Proc., 558, 399-402 (1999).
MRS Symp. Proc., 570, 309–313 (1999).
Appl. Phys. Lett., 76, 2740-2742 (2000).
MRS Symp. Proc., 623, 253-258 (2000).
MRS Symp. Proc., 666, F3.15.1-F3.15.6 (2001).
Int. J. Modern Physics B, 16, <1-2>, 173-180 (2002).
J. Appl. Phys., 91, 3547-3550 (2002).
Adv. Mater., 15, <15>, 1258-1262 (2003).

◆ **All Oxide p-n Heterojunction**
Appl. Phys. Lett., 75, 2851-2853 (1999).
Appl. Phys. Lett., 77, 475-477 (2000).
MRS Symp. Proc., 623, 283-288 (2000).
Electronics Letters, 36, <11>, 984-985 (2000).
J. Appl. Phys., 89, 5720-5725 (2001).
Key Engineering Materials, 214-215, 75-80 (2002).
J. Crystal Growth, 237–239, <1>, 496-502 (2002).
Appl. Phys. Lett., 82, 823-825 (2003).
Appl. Phys. Lett., 83, 1029-1031 (2003).
Adv. Mater., 15, <17>, 1409-1413 (2003).
Thin Solid Films, 445, <2>, 317-321 (2003).
Appl. Phys. Lett., 87, 211107 (2005).
Appl. Phys. Lett., 89, 153502 (2006).

◆ **Homologous-$InGaO_3(ZnO)_m$**
Thin Solid Films, 411, <1>, 147-151 (2002).
MRS Symp. Proc., 747, V2.6.1-V2.6.6 (2003).
Adv. Func. Mater., 13 <2>, 139-144 (2003).
Science, 300, 1269-1272 (2003). ★
Thin Solid Films, 445, <2>, 322-326 (2003).
Appl. Phys. Lett., 85, 1993-1995 (2004).
MRS Symp. Proc., 811, E2.9.1-E2.9.6 (2004).
J. Appl. Phys., 95, 5532–5539 (2004).
J. Ceram. Soc. Japan, Suppl.112-1, PacRim5 Special Issue, 112, <5>, S602-S609 (2004).
Thin Solid Films, 486, <1-2>, 28-32 (2005).
J. Ceram. Soc. Japan, 114, <2>, 147-154 (2006).
Crystal Growth & Design, 6, <11>, 2451–2456 (2006).
Thin Solid Films, 496, <1>, 64-69 (2006).

◆ **a-$InGaZnO_4$ (a-IGZO)**
MRS Symp. Proc., 623, 291-296 (2000).
Phil. Mag. B, 81, <5>, 501-515 (2001).
Nature, 432, 488-492 (2004). ★
Thin Solid Films, 486, <1-2>, 38-41 (2005).
Appl. Phys. Lett., 89, 112123 (2006).
MRS Symp. Proc., 928, GG10-04 (2006).
Jpn. J. Appl. Phys., 45, 4303-4308 (2006).
ECS Trans., 3, <8>, 293-300 (2006).
Phys. Rev. B, 75, 035212 (2007).
Appl. Phys. Lett., 90, 242114 (2007).
J. Soc. Info. Display, 15, <11>, 915-921 (2007).
SID Symp. Dig. Tech. Papers, 38, 1830-1833 (2007).

◆ **Proposal & Review on In-Ga-Zn-O Oxide Semiconductors**
J. Non-Cryst. Sol., 198–200, 165-169 (1996).
[16th-ICANS at Kobe, 1995.09.04-08]
J. Non-Cryst. Sol., 203, 334-344 (1996).
J. Non-Cryst. Sol., 227–230, 513–516 (1998).
Phil. Mag. Lett., 79, <9>, 755-761 (1999).
J. Am. Ceram. Soc., 82, <12>, 3330-3336 (1999).
MRS Bulletin, 25, 28–36 (2000).
MRS Symp. Proc., 623, 235-243 (2000).
J. Electroceramics, 4, 407–414 (2000).
Rev. Sci. Instrum., 72, 3340-3343 (2001).
Vacuum, 66, <3–4>, 419-425 (2002).
Solid-State Electronics, 47, <12>, 2261-2267 (2003).
MRS Symp. Proc., 796, V1.1.1-V1.1.12 (2003).
Thin Solid Films, 445, 193-198 (2003).
Materials Today, 7, <6>, 42-51 (2004).
Int. J. Appl. Ceram. Technol., 1, <2>, 106-118 (2004).
Microelectron. Eng., 72, 294–298 (2004).
Microelectron. Eng., 73–74, 620-626 (2004).
Int. J. Appl. Ceram. Technol., 2, <4>, 285–294 (2005).
Bull. Chem. Soc. Jpn., 79, <1>, 1-24 (2006).
J. Non-Cryst. Sol., 352, 851-858 (2006).
J. Electroceramics, 17, 267–275 (2006).
Thin Solid Films, 515, <15>, 6000-6014 (2007).
MRS Bulletin, 32, 242-247 (2007).

ed using ESR of Cu^{2+}, as the paper Hosono's insight shines. Also, as part of his research on amorphous chalcogenides, at the International Conference on Amorphous Semiconductors in Prague around 1987, Kawazoe presented his own view, different from the VAP (Valence Alternating Pair) model, in the presence of Professor Sir Nevill Francis Mott, who was awarded the Nobel Prize in Physics in 1977. However, it finished without any questions, and in the end, Kawazoe recalls that the three series of papers[123)-125)] that he claimed met with failure[120)]. Kawazoe's presentation at this international conference is very similar to the echo of Hosono's presentation at the same conference in 1995, as described below. Their every step as two researchers is as if they were walking together on the same railroad tracks. It certainly must have been a very painful presentation for Kawazoe. However, in the review paper[126)], "30 years of the research on amorphous semiconductors and future problems", it is described as follows: "To this day, there are still some who dispute the above theory of charged defects based on negative effective electron correlation energy, and in a sense, it can be said that the issue is still unresolved". Therefore, the author would like to point out that there is a literature that acknowledges the existence of Kawazoe's claim at that time as a different view.

3.1.3 N-Type Oxide Semiconductors, $MgIn_2O_4$ and β-Ga_2O_3, which Arose from the Concept "Conductive Insulator"

After Kawazoe was appointed professor at the Research Laboratory of Engineering Materials at Tokyo Tech in 1990, he finished the pending empirical paper on n-type conduction in In_2S_3[127)], and made a major shift in the laboratory's strategy from glass to the exploration of crystalline electronic functional materials, considering carrier density and electron mobility by doping as the parameters independent of the energy band gap (E_g) described in the textbook, for the classification of solids, thus focusing on a total of 3 independent parameters. Kawazoe coined the unique term "Conductive Insulator"[121)] because materials with high electron mobility could be present even among insulators with large E_g, or insulators with high electron mobility can be fabricated by doping, etc. This name is indeed interesting.

Considering the limitation of classifying solids based only on energy band gap from the conventional perspective of solid-state physics, Kawazoe introduced the concept of "Doping Science" and started joint research with Hosono and Naoyuki Ueda et al. of the Institute of Molecular Science around 1994[128)-131)]. In the initial stages, they developed $MgIn_2O_4$ with n-type conductivity and demonstrated the control of electrical conduction properties through the introduction of oxygen defects[1), 2), 8), 9)] and ion implantation (H^+, Li^+)[3)-7), 10), 11)].

Furthermore, Kawazoe and Hosono started their research on doping for materials with wider band gaps than $MgIn_2O_4$ (E_g ~ 4 eV). One of the researched materials was β-Ga_2O_3, a transparent material with an ultra-wide gap (E_g ~ 4.9 eV) and a wavelength up to around 250 nm. The goal is to transform this oxide into an n-type electrically conductive oxide by doping. The team grew single crystals of that oxide using the floating zone method, demonstrating that the conductivity can be changed by 10 orders of magnitude by controlling the oxygen partial pressure during post-annealing and that with Sn doping (3 mol%), a system showing high electrical conductivity almost equivalent to that of low oxygen partial pressure annealing can be obtained even when annealing in oxygen. The team successfully demonstrated that their concept of a doping method for wide-gap oxides was correct, thereby opening the door of "Doping Science" for oxides with wide gaps successfully[31)-35)].

3.1.4 Creation of P-Type Oxide Semiconductor, $CuAlO_2$

As mentioned above, Kawazoe and Hosono wanted to scientifically put an end to the mystery of what was being promoted as a tacit understanding that "Among materials that were normally classified as semiconductors until now, the pure ones are close to insulators, but doping can significantly improve their electrical conductivity; therefore, they can be classified as semiconductors", which has been a major motivation in the exploration of materials for a series of wide-gap oxide semiconductors. The way this issue is presented is very important and seems to be a quest for truth from a truly simple perspective, without relying on textbooks.

Kawazoe and Hosono then reconsidered the design of p-type oxide semiconductors, which had remained a challenge. If oxides are seen as ionic crystals, they are insulators because the electrons are localized in the highly electronegative oxygen anion ($2p^6$ orbital), forming the valence band maximum. Therefore, their design concept was to add some modulation to the valence band's upper end and consider a means of delocalizing the electronic state at the upper end of the valence band. As a delocalization strategy, Kawazoe and Hosono considered that if a metal cation with a closed-shell structure were brought to the same energy position as the oxygen 2p electron, significant hybridization would occur between the two, leading to delocalization. The challenge was focused on the selection of metal cations. Kawazoe and Hosono decided to proceed with the research under this material design because, among metal cations with an electron configuration of $(n-1)d^{10}ns^0$ (n = principal quantum number), the energy of the d^{10} electrons of Cu^+, Ag^+, Au^+, etc., is close to that of the oxygen $2p^6$ electrons. This guideline is a concept that also applies to Cu_2O, which has long been known as a p-type conductive oxide. When the crystal structure of Cu_2O was considered again, the Cu^+ ions were surrounded by oxygen O^{2-} ions in a tetrahedral configuration, similar to the sp^3 hybrid orbital, and it was considered to be highly unlikely that lone pairs of electrons would be generated. In other words, Kawazoe and Hosono thought that they could delocalize the electrons at the valence band maximum. In addition, since there was a concern about the narrowing of the band gap due to wider band dispersion when Cu^+ ions are close to each other in 3D space, Kawazoe et al. considered the introduction

of low-dimensionality into the crystal structure. As a result, $CuAlO_2$ with a delafossite-type crystal structure was selected as a candidate that satisfied all the above conditions[132), 133)]. The crystal structure is a 2D structure in which Cu^+ and AlO_2^- are stacked in alternating layers along the c-axis, and Al^{3+} constitutes a 2D surface that shares an edge with the AlO_6 octahedron. The distance between 2 Cu^+ ions on both sides of the AlO_6 octahedron is decided based on the spatial size of the AlO_6 octahedron. Furthermore, if we focus on the oxygen ion O^{2-}, it is surrounded by three Al^{3+} ions and one Cu^+ ion in a regular tetrahedral configuration. The foresight to conjure up and the ability to execute such materials design conditions when high-precision first-principles calculations like today were not available are very noteworthy. This is how the world's first p-type oxide semiconductor, $CuAlO_2$ ($E_g \sim 3.5$ eV), was born[25), 26)]. The reason why this research outcome was adopted in the *Nature* paper must have been because this result led to a series of research results, namely, the guideline for material design for p-type semiconductors, which was a challenge for a long time, and the selection of specific crystals conforming to the guideline, and demonstration of the properties of p-type semiconductors through thin film fabrication, and also because this research result was highly acclaimed as a paper that proved to be a major starting point for future material development.

Following this design guideline, $CuGaO_2$ ($E_g \sim 3.6$ eV) with the same delafossite type was discovered as a p-type oxide semiconductor[39), 96)], and $SrCu_2O_2$ ($E_g \sim 3.3$ eV) was also found[27), 28)]. The latter is a magnificent p-type oxide semiconductor induced by substitutional doping of Sr^{2+} sites with low-valent K^+, demonstrating the importance of doping in p-type oxide semiconductors. In addition, $CuInO_2$ also functions as an oxide semiconductor, and interestingly, $CuInO_2$ was found to be a p-type semiconductor when doped with Ca and an n-type semiconductor when doped with Sn[36)]. It is also significant that this interesting characteristic was immediately used to demonstrate the characteristics of p-n homojunction diode using the same mother crystal ($CuInO_2$)[37), 38)]. On the other hand, it was also demonstrated that $AgInO_2$, the same delafossite-type crystal, when doped with about 5% Sn, forms a highly transparent ($E_g \sim 4.4$ eV) n-type semiconductor in a wide range of visible light, with its electrical conductivity improved by several orders of magnitude[29), 30)].

3.1.5 PN Junction Composed of Oxide Semiconductors

After the discovery of these p-type oxide semiconductors, the next step was the demonstration of p-n junctions. A p-n junction is the minimum required device to be considered a "semiconductor". Hosono and Kawazoe et al. demonstrated the diode characteristics of a fully oxide-based transparent n-ZnO/p-$SrCu_2O_2$ p-n junction, including electrodes[53)]. Later, after changing the electrode on the $SrCu_2O_2$ side to Ni, they successfully completed a light-emitting diode that emits light at a wavelength of around 382 nm by current injection[54)-59), 134), 135)]. In particular, the degree of perfection of the heteroepitaxial growth technology[57)-59)] on yttrium-stabilized zirconia (YSZ) substrates is also considered to have contributed significantly to the success of the light-emitting diode (LED). Regarding this p-n junction, in addition to the n-ZnO/p-$SrCu_2O_2$ combination, Hosono's laboratory conducted considerable research and accumulated technology for all-oxide junction configurations, such as n-ZnO/p-$ZnRh_2O_4$[60)], n-$InGaZn_5O_8$/p-LaCuOSe[64)], and the simplest p-n heterojunction n-ZnO/p-NiO[61), 63), 65)].

3.1.6 The Dawn of Amorphous Oxide Semiconductors

Up to now, I described the events that led to the success in demonstrating p-n junctions by fabricating high-quality oxide thin films using epitaxial thin films in line with the current technological trends in oxide electronics. In this section, I will unfold the story behind amorphous oxide semiconductors. The study of amorphous materials is positioned directly opposite to the epitaxial single-crystallization technique from the perspective of materials design and fabrication. According to the author's understanding based on old knowledge, the density of states in an energy band is tailed near the band edge because the long-range order established in the crystals is missing, and the periodic potential is disturbed. The electron density tail above the Valence Band Maximum (VBM) and below the Conduction Band Minimum (CBM) is often called the band tail (tail region). At the same time, the physical image of the electron is also called "Anderson localization", in which the movement of electrons is significantly restricted (localized)[136)-138)]. In other words, from the point of view of solid-state physics, the mobility of electrons in amorphous semiconducting materials is considered to be much lower than that in crystals since it is considered that electrons are no longer transferred by electron carrier in the crystalline bands but by the Variable Range Hopping (VRH) mechanism. In any case, when making semiconductor devices with amorphous materials, cleaning the interface and topmost layers is considered to be difficult. Because of the numerous dangling bonds, etc., the device will have many electronic levels in the band gap and a band tail above the VBM and below the CBM, which is generally considered to result in a significant degradation of device characteristics. In other words, controlling the Fermi levels in amorphous semiconductors is difficult. The only exception is hydrogenated amorphous silicon, in which dangling bonds can be controlled to a significant extent as they combine with hydrogen, thus making it possible to control the Fermi levels close to the band edge. However, since the density of states at the band tail could not be reduced significantly, moving the Fermi levels beyond the band edge was impossible. Therefore, band conduction did not occur, and the mobility remained below 1 cm^2/Vs.

One of the approaches could be that the magnitude of the density of states in the tail region is considered to correlate with the bond angles of chemical bonds and is considered to be sensitive to covalent properties and insensitive to ionic properties; the density of states in the tail region is an order of

magnitude lower in oxides with strong ionic properties, and as a result, it is inferred that band conduction is possible in oxides such as IGZO presented here.

Here, I will briefly touch upon a few past papers on amorphous oxides or oxide glass considered for their electrical conductivity. The electrical conductivity was discussed for the first time in a paper by E. P. Denton et al. on Vanadium-based oxide glass (V_2O_5-MO_x: M=P, Te, Ba, Ge, As, Pb) published in 1954[139]. Although the research[140)-142)] on this semiconductor glass has gained momentum since then, today, the interest has waned since its electrical conduction is by a VRH mechanism, and its mobility is as low as 10^{-4} cm^2/Vs or lower. V_2O_5 exhibits a lack of transparency in the visible region due to absorption by d-d transitions of V^{4+}, and difficulty in improving the conductivity is considered to be the reason. For details, please refer to Munakata's commentary[143), 144)]. However, since this material also seems to exhibit somewhat high transparency in the infrared region, it would be interesting to develop different applications of this glass from today's perspective, similar to chalcogenide glass[145)]. Later, in the early 1990s, a paper on amorphous Indium oxide (a-InO_x) was published by J.R. Bellingham et al. of Cavendish Laboratory in the UK[146)-148)]. Thus, although papers were presented on the electrical conductivity of amorphous oxides, an atmosphere that would lead to significant progress in the development of materials through carrier control or sow the seeds of technological trends had not yet been created.

In contrast, Hosono's experience cultivated in the field of inorganic glass and amorphous chalcogenide materials led him to view oxides as transparent wide-gap semiconductors. He had a firm vision that, despite being amorphous, the oxides could function as semiconductors by doping carriers with certain methods, such as substitution by heterovalent metals, introduction of oxygen defects, and ion implantation, and the author believes that this vision may have expanded as research continued. The experiment results on $AgSbO_3$ by Masahiro Yasukawa, a student at that time provided a major hint toward this steadfast vision[21)-23)]. A published interview article[149)] with Hosono includes the following statement.

> "I started my research on transparent amorphous oxides from the time the results of the experiment by Masahiro Yasukawa, currently a professor at the Kochi National College of Technology's Department of Materials Science and Engineering, were obtained. When looking for a new crystalline transparent oxide conductor, I discovered that an amorphous thin film of silver antimonate ($AgSbO_3$) had electron mobility not too different from crystals. ~ Partially omitted ~ At that time, it was common knowledge that electrons would not move easily (electricity would not flow) unless the atoms were arranged neatly in a material, such as crystalline silicon (Si). Although amorphous silicon was being actively researched, it was known that it is much more difficult for electrons to move in amorphous silicon than crystalline silicon. Also, it was not known that amorphous oxides can be excellent semiconductors. Therefore, even if we assume that materials were created using amorphous oxides for use as semiconductors, it would have been normal not to pursue this further, thinking, "The characteristics would be much worse than crystals anyway". However, I had a gut feeling, "This is it!" Thinking about why this phenomenon occurs, I immediately came up with a model."

In particular, according to the paper[22)] that describes the discovery of amorphous $AgSbO_3$, the electrical conductivity improves by 4 orders of magnitude from the as-deposited film to when annealed at 500°C in oxygen, and although crystallization occurs at 675°C and the electrical conductivity improves by one order of magnitude, looking over the dynamic range of electrical conductivity, I can say that there is not much difference between amorphous and crystalline materials in terms of their electrical conductivity. Although annealed in oxygen, the amorphous state is maintained at 500°C as observed by X-rays. At the same time, a certain amount of oxygen defects are naturally introduced, which are considered to generate carriers and significantly improve conductivity. In addition, it was inferred that the antibonding orbital between $4d^{10}5s^0$ of Ag^+ or $4d^{10}5s^0$ of Sb^{5+} and $2p^6$ of O^{2-}, most likely contributed to the conduction mechanism. The experimental data by Yasukawa are shown in Table 3.2, and it is believed that Hosono immediately grasped the essence of the data with his keen insight, which he considered the key subject of important future exploratory research.

Table 3.2 In the case of fabricating sputtered $AgSbO_3$ thin films, carrier density, electron mobility and conductivity at room temperature, respectively for amorphous phase annealed at 500°C in oxygen gas and multi-crystalline phase annealed at 675°C in oxygen gas[22)]

Sample Phase	As-Deposited Film	Amorphous (500°C annealed in O_2)	Polycrystalline (675°C annealed in O_2)
Carrier Concentration [cm^{-3}]	-----	2.7×10^{17}	2.9×10^{18}
Mobility [$cm^2V^{-1}s^{-1}$]	-----	6.7	7.5
Conductivity [$\Omega^{-1}cm^{-1}$]	$\sim 1 \times 10^{-5}$	0.29	3.5

Just as Hosono was inspired by the data on $AgSbO_3$, Kawazoe, the head of the laboratory, came across a paper on a "certain material" and became seriously interested in the idea of imparting electrical conductivity to amorphous oxides. According to a column by Kawazoe[121], this happened when he came across a paper[150] describing "photoconduction in $CdO \cdot SiO_2 \cdot Na_2O$ photochromic glass". Following this, Kawazoe and Hosono's laboratory presented a paper[17] on the electrical conductivity of amorphous Cd_2GeO_4 which was the second material after $AgSbO_3$ (Actually speaking, if the notation in the paper is followed, the name should have been $2CdO \cdot GeO_2$ or Cd-Ge-O; however, the name that reflects the spinel-type structure of the mother crystal is mentioned in this document, similar to $AgSbO_3$). The first author of that paper was Hosono, and it is presumed that the importance of the research on amorphous oxide semiconductors was conveyed to many laboratory members, including Kawazoe, through this paper compiled by Hosono on amorphous Cd_2GeO_4. In the case of amorphous $AgSbO_3$, the introduction of oxygen defects by post-annealing improved its conductivity by 4 orders of magnitude while maintaining the amorphous state, whereas in the case of amorphous Cd_2GeO_4, ion implantation dramatically improved the conductivity by 10-11 orders of magnitude. During his experience as a corporate employee over a long period, the author has seen ion implantation experiments being mostly used exclusively for silicon, and samples of oxides, etc., are considered a source of contamination when just placed in the chamber; therefore, it is considered extremely difficult to obtain approval from the management division for ion implantation at private companies handling semiconductors. Even under such an environment, it is truly significant that Hosono et al. conducted the research in cooperation with researchers who were familiar with ion implantation. Hosono et al.'s data indicate that conductivity dramatically improves by introducing carriers, as shown in Table 3.3.

It was inferred that the antibonding orbital between $4d^{10}5s^0$ of Cd^{2+} or $3d^{10}4s^0$ of $Ge^{4+}$and $2p^6$ of O^{2-} had most likely contributed to the conduction mechanism, and the optical band gap was also estimated to be 3.4 eV, larger than that of $AgSbO_3$. From these two examples, it is considered that the $(n-1)d^{10}ns^0$ electronic state, which will be discussed later, was presumably viewed to be extremely important.

Embarking on such an experiment of ion implantation into an amorphous oxide is considered a solid step toward amorphous transparent conducting oxides. The research results on the conductivity of these two amorphous materials likely validated the design guidelines and direction adopted by Kawazoe and Hosono et al., and marked a significant stride forward for the entire laboratory. Narushima et al.[18)-20)] subsequently took over the research.

Similar research was conducted on Cd_2PbO_4, which joined the ranks of amorphous conductive materials[24]. As shown in Table 3.4, even the film deposited by sputtering had a very high conductivity of 180 Scm^{-1}, a carrier density of $1x10^{20}$ cm^{-3}, and a mobility of 9 cm^2/Vs. When annealed to 250°C, at which the amorphous state is maintained, conductivity and carrier density were twice as high as the values for the as-deposited film, respectively. The reason is considered to be due to the introduction of oxygen defects. Simply put, this conductivity value is still 5 orders of magnitude lower than that of gold, silver, and copper. However, this is a good conductivity value, much more than 10 orders of magnitude higher than ordinary colorless transparent glass.

Thus, particularly the fact that conductivity can be significantly improved or controlled by carrier doping of the 3 amorphous oxides a-$AgSbO_3$, a-Cd_2GeO_4, and a-Cd_2PbO_4, must have undoubtedly helped Hosono to confirm his "Working Hypothesis".

Table 3.3 In the case of fabricating sputtered amorphous Cd_2GeO_4 thin films, carrier density, electron mobility and conductivity at room temperature, respectively for Li^+ ion implantation and H^+ ion implantation[17].

Sample Phase	As-Deposited Film	Li^+	H^+
Carrier Concentration [cm^{-3}]	-----	1×10^{19}	7×10^{18}
Mobility [$cm^2V^{-1}s^{-1}$]	-----	6	4
Conductivity [$S\ cm^{-1}$]	$\sim 3 \times 10^{-9}$	13	6

Ion Implantation Conditions:
- $80KeV, 1x10^{16}cm^{-2} + 160KeV, 1x10^{16}cm^{-2}$ for Li^+
- $40Kev, 1x10^{16}cm^{-2} + 70KeV, 1x10^{16}cm^{-2}$ for H^+

Table 3.4 In the case of fabricating sputtered amorphous Cd_2PbO_4 thin films, carrier density, electron mobility and conductivity at room temperature, respectively for as-deposited phase and phase annealed at 250°C[24].

Sample Phase	As-Deposited Film	250°C-Annealed Film
Carrier Concentration [cm^{-3}]	1×10^{20}	2×10^{20}
Mobility [$cm^2V^{-1}s^{-1}$]	9	10
Conductivity [$S\ cm^{-1}$]	200	400

A few years later, Hosono measured the X-ray radial distribution function for the a-Cd_2GeO_4 thin film, determined its atomic configuration by analysis using the reverse Monte Carlo (RMC) method, and calculated the electronic density of states (DOS) from cluster calculations, and also conducted direct and inverse photoelectron spectroscopy analysis in parallel[20]. Here, "direct" photoelectron spectroscopy is ultraviolet photoelectron spectroscopy (UPS), which measures the density of electronic states in an occupied state, and "inverse" is a technique that measures the electronic density of states in the conduction band. By comparing the DOS derived from the calculations and the DOS measured by the direct and inverse photoelectron spectroscopy, it was shown that the bottom of the conduction band responsible for n-type conduction mainly

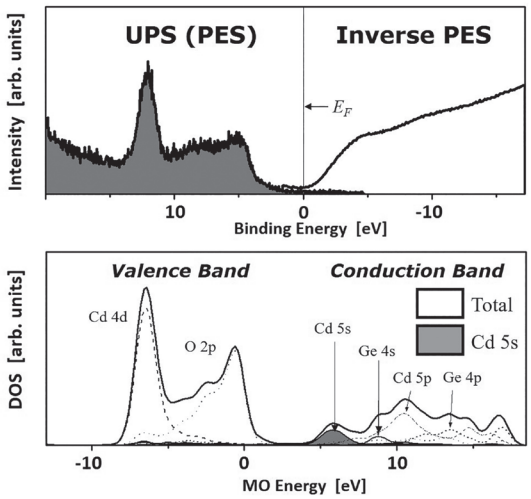


Fig. 3.1 Calculated DOS for amorphous cluster and its partial components along with the observed ultraviolet photoelectron (PE)-ultraviolet inverse photoelectron (IPE) spectrum of amorphous Cd_2GeO_4 film. Drawn was each MO level convoluted by Gaussian function (dashed line).
(Published three figures in reference (20) revised a little by courtesy of Prof. Hosono.)

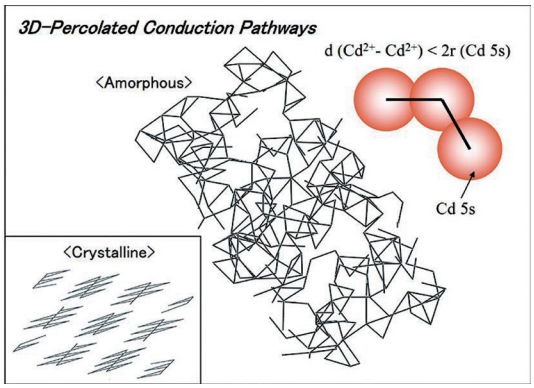


Fig. 3.2 Cd-Cd correlations extracted from the resulting reverse Monte Carlo simulation (RMC) model for amorphous Cd_2GeO_4. The representation is 1/8 of the actual RMC box.
When the neighboring Cd-Cd separation is within the sum (0.36 nm) of two Cd^{2+} 5s-orbital radii, a pair of Cd ions is connected by a line. Note that the 3D-percolation pathways for electrons are seen in the whole configuration space. The inset is the figure drawn by the same procedure for the crystal. (Published three figures in reference (20) revised a little by courtesy of Prof. Hosono.)

consists of a three-dimensionally connected Cd5s orbital. The two main figures related to the results of this research are Fig. 3.1 and Fig. 3.2, respectively.

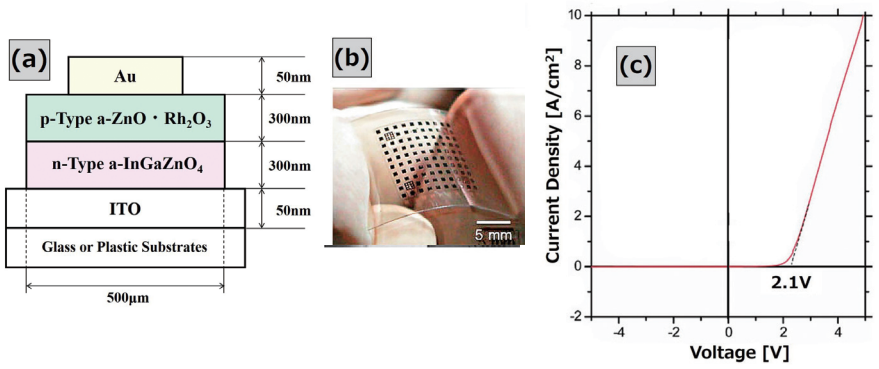
One can say that the research results demonstrate the "Working Hypothesis" and the "Design Guideline" of transparent amorphous oxide semiconductors based on scientific evidence. It is an important and significant research result that has grasped the essence of amorphous oxide semiconductors using direct and inverse photoelectron spectroscopy over several years after discovering the 3 aforementioned amorphous materials.

3.1.7 Creation of the PN Junction Device Composed of All Amorphous Transparent Oxides

During this period, semiconductor characteristics of several materials were being simultaneously confirmed, one of which was $ZnRh_2O_4$[40)-42), 62)] exhibiting p-type conduction, and another was amorphous $InGaZnO_4$[79), 80)] exhibiting n-type conduction. Satoru Narushima[151)] et al. of Hosono's group succeeded in creating the first ever amorphous $ZnRh_2O_4$, an amorphous oxide exhibiting p-type conductivity[62)]. However, this amorphous oxide, although amorphous, has a localized RhO_6 edge-shared structure and was therefore considered to be a d-t_{2g} type electrical conductor. The conductivity of amorphous $ZnRh_2O_4$ fabricated by sputtering was about 2 Scm^{-1}, and the band gap was about 2 eV.

Since the amorphous a-$ZnRh_2O_4$ was p-type, Hosono's group fabricated a p-n junction using a-$InGaZnO_4$, which had already been researched at this stage as an n-type amorphous oxide[62)]. The reason for choosing a-$InGaZnO_4$ as the n-type material was maybe because it was the most familiar material in the laboratory, and its characteristics were stable. Or it could also be a preliminary check, as Hosono had already planned to conduct demonstration experiments of transistors soon using this material. Since both p and n phases are amorphous oxides, the steepness of the electronic band at the junction interface is a concern; however, the film with stacked p-n layers, consisting of [Au/p-$ZnRh_2O_4$ (300 nm)/n-$InGaZnO_4$ (300 nm)/ITO] was fabricated on a glass substrate. After confirming the ohmic property of each electrode in advance, a rectification ratio of 3 orders of magnitude was successfully achieved. Fig. 3.3 shows the typical structure and characteristics of the film.

Since these amorphous devices can be deposited at room temperature, it is also considered that the advantage of dispersion being less likely to occur at the junction interface was inherently created, which must have been a major advantage of using the amorphous phase. In any case, this was a demonstration of the world's first p-n junction diode with all-amorphous oxide, which is a truly epoch-making and significant research outcome.



(a) p-$ZnRh_2O_4$/n-$InGaZnO_4$ heterojunction structure with all amorphous phases.
(b) The image photograph of all amorphous transparent pn-junction thin film devices created on a flexible plastic substrate.
(c) Current density (J)-voltage(V) characteristic of this pn-junction. The inset shows a logarithmic plot of the J-V characteristic. The device shows an on-off current ratio of 10^3 at ±5V.
(Published three figures in reference (62) revised a little by courtesy of Prof. Hosono.)

Fig. 3.3 Various data of the pn-junction device composed of all amorphous transparent oxide thin films.

Column: Introduction of Oxide Semiconductors Found during this Period and Status of Subsequent Research Developments

The following is a brief bulleted list of papers the author found interesting regarding the subsequent development of conductive oxides and oxide semiconductors discovered from 1992 to 2002.

◆ $MgIn_2O_4$ system:

Naoyuki Ueda, formerly a researcher at the Institute of Molecular Science and now working at the Ricoh Company, Ltd., has subsequently continued the development of this material and fabricated $MgIn_2O_4$-TFT[1), 2)]. Other research institutions have also reported papers related to transistors[3), 4)].

◆ β-Ga_2O_3 system:

A paper by Tippins in 1965 reported that this material has a very wide band gap and is photoconductive[5)]. In contrast, as mentioned above, Hosono's group inherited the technology from Naoyuki Ueda (2 papers: Reference No. 31 and 32 in this chapter) and Masahiro Orita (3 papers: Reference No. 33, 34, and 35 in this chapter), and then in 2006, 2 papers were published by then graduate student Kousuke Matsuzaki on transparent field-effect transistors using β-Ga_2O_3 (E_g^{op} = 4.9 eV)[6), 7)]. He chose Sn-doped material, changed the conventional YSZ substrate to the α-Al_2O_3 (sapphire) substrate, and fabricated field-effect transistors based on the heteroepitaxial growth technology while also paying attention to the substrate temperature and oxygen partial pressure control. However, the mobility was only about 0.05 cm^2/Vs.

Subsequently, Masataka Higashiwaki of the National Institute of Information and Communications Technology [NICT] greatly developed this material as a transistor characterized by an extremely high breakdown voltage, using the same β-Ga_2O_3 as the substrate. Though some relevant papers[8)-10)] and various information[11)-14)] are included, further details to introduce this material are beyond the scope of this systematic survey report. This series of research on Ga_2O_3-TFTs is a good example of how the seeds sown by Hosono's group have significantly blossomed in the form of achievements by Higashiwaki of NICT.

◆ $ZnGa_2O_4$ system:

The applied research on this material is being actively conducted in fields such as photovoltaic cells, etc., as a p-type wide band gap oxide semiconductor. The material also has applications as a photocatalyst and is gaining momentum gradually with several interesting papers[15)-17)].

◆ $AgInO_2$ system:

This material is being researched for its photocatalytic particles but has not yet reached a significant development[18), 19)]. On the other hand, the formation of uniform $AgInO_2$ hexagonal nanoplates with an average width of about 300 nm and thickness of 70 nm composed of (00l) facets was synthesized by hydrothermal synthesis. This research result is interesting, as the fine particles do not contain potassium ions, which are of concern as impurity ions[20)].

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3.2 Establishment of Technical Base of Epitaxially-Grown Single-Crystalline Thin Films and Introduction of a New Method called Reactive Solid-Phase Epitaxy

3.2.1 Oxide Electronics

Hosono's laboratory has also been refining its expertise in the field of single-crystalline thin-film technology, a field that allows for the maximum utilization of crystal characteristics. In other words, in oxide electronics[152], the team has been focusing on advancing epitaxial growth technology, which has shown significant improvement in the field of single-crystalline thin-film technology.

The names of several researchers come to my mind, who were active at the time when the fundamental research on high-temperature superconducting oxides had flourished, for example, the research team of Yoshichika Bando and Takahito Terashima of the Kyoto University Institute for Chemical Re-

search[153)-156)] who fabricated epitaxially-grown single-crystalline thin films (hereinafter abbreviated as epi-films) of high quality at that time by making full use of the reactive vapor deposition method, the research team of Ayahiko Ichimiya et al.[157)-160)] of Nagoya University who popularized Reflection High-Energy Electron Diffraction (RHEED), which enabled in-situ monitoring of film deposition, Shozo Ino[161)] of the University of Tokyo, who developed RHEED-TRAXS, which can perform elemental analysis simultaneously in a form that is integrated with RHEED, the research team of Hideomi Koinuma and Masashi Kawasaki[162)-164)] of Tokyo Tech, who were the first in the world to report the importance of ultra-smoothing of $SrTiO_3$ single-crystal substrates by top surface treatment in the field of single-crystal substrate technology for epitaxial growth, the research team of Masakazu Aono and Mitsuhiro Katayama[165), 166)] at RIKEN, who developed the Coaxial Impact-Collision Ion Scattering Spectroscopy (CAICISS), which enabled structural analysis of the topmost surface layers of compound semiconductors such as InAs, and Mamoru Yoshimoto[167)-170)] of Tokyo Tech, who applied the CAICISS technology to the structural analysis of the topmost surface of oxide single-crystal substrates such as sapphire, and paved the way for the fabrication of single-crystal substrates with clean topmost layer structures on an atomic scale. The technology mentioned above for epitaxially-grown single-crystalline oxide thin films and step processing technology for topmost layers of single-crystal substrates have functioned and evolved as a well-meshed gear and are, so to speak, sophisticated technological fields at an atomic scale with elements of Japanese specialty. Even today, there is no doubt that these technologies firmly establish the foundation of the technological field of oxide electronics.

3.2.2 Epitaxial Single-Crystalline Thin Films of ITO-Related Conductive Oxides

ITO thin films are the most well-known and put to practical application in the research on transparent conducting oxides, as also mentioned in Chapter 2. The above trend in oxide electronics also helped in the publishing of several technical reports on epitaxial thin films of ITO by a group led by Yuuzou Shigesato, a former employee of Asahi Glass and currently a professor at Aoyama Gakuin University in the mid-1990s[171)-173)]. Shortly thereafter, Hosono and Kawazoe of Tokyo Tech published papers on heteroepitaxial growth of In_2O_3 thin film[45)] and ZnO thin film[46)] on YSZ single-crystal substrates, respectively, which were co-authored by Masahiro Orita and Hiromichi Ohta et al. of HOYA, who were conducting joint research.

After research on inorganic and chalcogenide glasses, they conducted a wide range of research on n-type and p-type oxide semiconductors and several new amorphous oxide semiconductors, as a step toward new doping science. I am sure that under such circumstances, it must have been extremely challenging for them to promote research on epitaxial thin films in their laboratory, and they must have experienced considerable hardship.

Subsequently, Hosono got Hiromichi Ohta and Masahiro Orita of HOYA to participate in ERATO "HOSONO Transparent ElectroActive Materials Project" of the Japan Science and Technology Corporation (JST, currently the Japan Science and Technology Agency). The first research theme at that time is considered the epitaxial growth of ITO films on YSZ single-crystal substrates by the Pulsed Laser Deposition (PLD) method. The electrical resistivity of the ITO films obtained at a substrate temperature of 600°C was reported to be extremely low at 7.7×10^{-5} Ω.cm, and the transmittance in the visible region was as high as 85%[47), 48)]. The electrical conductivity of these ITO films is among the highest in the world. Ohta et al. in Hosono's group presented a report again on ITO epi-films on YSZ single-crystal substrates[51)]. Although the deposition temperature was high at 900°C, they again achieved a very low resistance of 1×10^{-4} Ωcm by the PLD method, taking into account the control of oxygen partial pressure during the deposition, and also reported that the (111) orientation of the ITO thin film is more crystalline than (100) orientation, based on X-ray locking curve, etc. Around the same time, Shigesato et al. reported epitaxial growth of non-doped In_2O_3 and ITO thin films on YSZ substrates using MBE equipment[174)]. The difference from Shigesato's paper published a few years ago was that the deposition method was Molecular Beam Epitaxy (MBE). The surface morphology is shown to be significantly different with and without Sn. The reported electrical properties were carrier density 6.5×10^{20} cm^{-3} and specific resistance 2×10^{-4} Ω.cm at Sn-2.6% doping, indicating that the doping effect was 81%. Meanwhile, Hosono's group working on ERATO had also attempted epitaxial growth for various types of functional oxides other than ITO[50)]. It can be inferred that Hosono's group as a whole had systematically accumulated the technology for the formation of epitaxial single-crystalline thin films of transparent oxide semiconductors step by step.

The development of epitaxial thin film technology for transparent conducting oxide thin films was not limited to Shigesato's or Hosono's group working on JST-ERATO. It was also a fundamental technological trend in oxide electronics, and similar research reports started emerging internationally after 2000. For example, Jean-Marie Tarascon et al. from France fabricated typical homologous phase thin film compound $In_2O_3(ZnO)_m$ ($m = 2 \sim 15$) on glass substrates by the PLD method. Although it is not considered to be an epi-film because a glass substrate is used, the temperature dependence of the resistivity and the optical properties reported indicate a degenerate semiconductor-like behavior showing an almost metallic-like appearance regardless of the value of m and that there is a gradual decline in the electron mobility as the value of m increases[175)]. Around the same time, Naoki Ohashi's group at the National Institute for Materials Science (NIMS) reported fabricating epitaxial thin films of In-Zn-O homologous phase[176)]. His group belonged to the same National Institute for Research in Inorganic Materials as Noboru Kimizuka, who have been conducting fundamental research on homologous oxides and promoted the research using c-face sapphire

as a substrate and $In_2O_3(ZnO)_5$ and ZnO as targets. The investigation was conducted by varying the substrate temperature up to 600°C, and post-annealing was performed at 800°C in various atmospheres of O_2, Ar, and N_2. (00$\underline{2}$1) and (00$\underline{2}$4) diffractions appear by this post-annealing in oxygen, and the importance of the oxygen atmosphere during the film deposition and the annealing process is described based on TEM electron diffraction images, and X-ray pole figures, etc., which show highly oriented transparent conducting films.

3.2.3. Reactive Solid-Phase Epitaxy

While research reports on epitaxial growth, including such highly oriented films, were booming, a method to fabricate better quality epi-films of homologous oxides was reported independently by Hosono's group working on ERATO and Naoki Ohashi's group at the National Institute for Materials Science (NIMS) in 2002. The common technology is the process technology in which an ultra-thin seed layer of a characteristic oxide layer is provided as a substrate template layer for epitaxial growth followed by post-annealing treatment, and both can be described as single-crystalline thin-film technology that uses the driving force of crystallization by solid-phase reactions. The method was named "Reactive Solid-Phase Epitaxy (R-SPE) Method" by Hosono's group working on ERATO[66)-68), 73), 74), 76), 104)], in which a ZnO layer with a thickness of merely 2 nm ~ 200 nm was deposited (substrate temperature = 600°C) before epitaxial growth to form the base layer. It is needless to say prior research[45)] on epitaxial ZnO thin films was utilized in the ZnO base layer deposition technology. On the other hand, Ohashi's group at NIMS[177), 178)] named the method as "Self-Buffer Layer Method". In the Self-Buffer Layer Method, a layer of $In_2O_3(ZnO)_5$ having the same composition as the film to be deposited is deposited to a thickness of 10 nm before epitaxial growth and then annealed at 400°C in a chamber to prepare the base layer. The Reactive Solid-Phase Epitaxy method was an interesting method devised by Hiromichi Ohta of Hosono's group[179)].

The process of the Reactive Solid-Phase Epitaxy Method is explained briefly according to Fig. 3.4., first, a ZnO template layer with a thickness of approximately 2 ~ 200 nm is deposited on a YSZ (111) single-crystal substrate under 600°C substrate temperature. [Step 1] Next, about 150 nm of $In_2O_3(ZnO)_5$ phase is deposited at room temperature. [Step 2] Another YSZ single-crystal substrate is placed on top of the bilayer thin film, covering it like a lid. This cover is also meant to prevent evaporation of ZnO and In_2O_3. [Step 3] Finally, heat treatment is performed in an electric furnace at 1450°C in air for about 30 minutes. [Step 4] The process is completed by cooling the film to room temperature and removing it from the electric furnace. [Step 5] Ohta, in particular, who devised the Reactive Solid-Phase Epitaxy Method, has carefully and comprehensively compiled this epitaxy technique in his papers[68), 104)]. Ohta was later awarded the 59th Progress Award from the Ceramic Society of Japan in the spring of 2005[76)].

On the other hand, Naoki Ohashi's group at NIMS laid an $In_2O_3(ZnO)_5$ template layer of thickness 10 nm on a single-crystal sapphire (0001) substrate, annealed it in a sputter chamber at a substrate temperature of 400°C, and then fabricated a 500 nm epitaxial thin film of $In_2O_3(ZnO)_5$ homologous oxide on it by sputtering. The X-ray pole figures and cross-sectional TEM lattice images[177), 178)] clearly show that crystalline thin films with very high in-plane orientation were obtained. The research results on this Self-Buffer Layer Method by Ohashi's group are considered equally significant as the Reactive Solid-Phase Epitaxy Method developed by Hosono's group in terms of materials science, and it is interesting to note that both methods were devised around the same time.

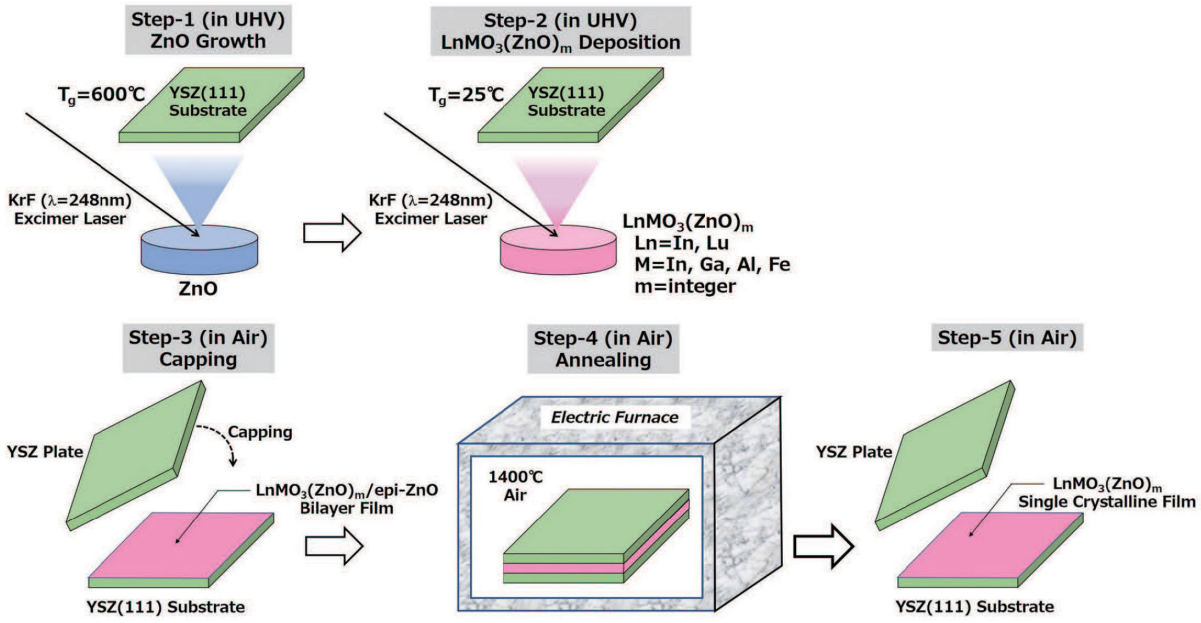

Fig. 3.4 Fabrication process of single crystalline $In_2O_3(ZnO)_5$ films grown by the reactive solid-phase epitaxy method.
(Prepared by the author based on the figure in reference (68).)

3.3 Hosono's Working Hypothesis

Hosono's Working Hypothesis on materials design for transparent materials, i.e., have a wide gap and that maintain high conductivity even in an amorphous state, was first conveyed to the world in a presentation at the 16th International Conference on Amorphous Semiconductors (ICAS16) held in Kobe, Japan, in September 1995. The contents were subsequently summarized in a paper in the following year's *Journal of Non-Crystalline Solids*[91]. This paper was published just around the time when experiments on carrier control by doping 3 kinds of amorphous oxides, a-$AgSbO_3$[22], a-Cd_2GeO_4[17], and a-Cd_2PbO_4[24], as amorphous materials, were being carried out simultaneously in Kawazoe and Hosono's laboratory. Since Hosono had determined that carrier control was almost certainly possible, Hosono presumably named his paper "Working Hypothesis". The author believes this is equivalent to establishing the conditions for exploring transparent amorphous oxide semiconductors.

In response to the oral presentation at the international conference, the audience showed hardly any interest in new amorphous oxide semiconducting materials (including the old stereotype of glass) as alternatives to amorphous silicon, as it was the heyday of amorphous silicon. Hosono's bitter memories of this are mentioned in several interview articles and technical journals of companies[180)-183)]. The author empathizes with the following metaphor used by Hosono in the interview article[180)].

> "At that time, silicon was at the center of attention. For example, silicon is Ginza. Each street is named clearly and has a distinct street number. There are many famous stores. Similarly, our academic system is also clearly defined. Therefore, there were many themes to research. Since germanium was replaced by silicon as a semiconductor in the 1940s, the research progressed rapidly and went so well that very few people considered semiconductors other than silicon. With silicon at the center, our glass-based amorphous oxides were the materials on the corner."

The contents of Hosono's presentation at ICAS16 in 1995 were reported again in the same journal in 1996 under a different title, "Novel oxide amorphous semiconductors: Transparent conducting amorphous oxides", in which 3 types of amorphous oxides (a-$AgSbO_3$, a-Cd_2GeO_4, a-Cd_2PbO_4) were reported as promising new wide-gap oxide semiconductors[92)]. It was again proposed that composite oxides composed of 15 heavy metal ions are important for exploring wide-gap oxide semiconductors. In other words, the electron orbitals of heavy metals with a principal quantum number n of 4 or more must be left vacant when ionized to include spherically symmetric s orbitals. The s orbital becomes a strong candidate because as the atomic number increases, implying a heavier element, the radius of the s orbital extends, leading to a greater overlapping component of the s orbital. The electron configuration of the ions of the 15 metallic elements is shown in Fig. 3.5.

Metal Ions	Electron Configuration
Cu (1+)	$3d^{10}\ 4s^0$
Zn (2+)	$3d^{10}\ 4s^0$
Ga (3+)	$3d^{10}\ 4s^0\ (4p^0)$
Ge (4+)	$3d^{10}\ 4s^0\ (4p^0)$
As (5+)	$3d^{10}\ 4s^0\ (4p^0)$
Ag (1+)	$4d^{10}\ 5s^0$
Cd (2+)	$4d^{10}\ 5s^0$
In (3+)	$4d^{10}\ 5s^0\ (5p^0)$
Sn (4+)	$4d^{10}\ 5s^0\ (5p^0)$
Sb (5+)	$4d^{10}\ 5s^0\ (5p^0)$
Au (1+)	$5d^{10}\ 6s^0$
Hg (2+)	$5d^{10}\ 6s^0$
Tl (3+)	$5d^{10}\ 6s^0\ (6p^0)$
Pb (4+)	$5d^{10}\ 6s^0\ (6p^0)$
Bi (5+)	$5d^{10}\ 6s^0\ (6p^0)$

Fig. 3.5 Electron configuration of 15 metal ions that meet the requirements to be candidates as transparent amorphous semiconducting oxides.
The electron configuration in parentheses ( ) means that electrons are missing from the outermost p-orbitals. In fact, the larger s-orbitals of the same outermost orbitals are thought to dominate the large orbital overlap.

This "Hosono's Working Hypothesis" is very intuitive and easy to understand, and when one looks back over the actual experimental results, the material design seems to "make sense." The following is a bulleted summary of the author's understanding of this situation.

Hosono's Working Hypothesis

- Focusing on the oxygen that makes up the oxide, most oxides tend to have a generally wider band gap because of the lower energy level of the 2p electron orbital of the oxygen that makes up the valence band maximum (VBM).
  In other words, since the transparent wavelength range is expected to be extended, oxides are prime candidates.
- To maintain high electron mobility, it is important that heavy metal ions with large orbital radii of the outermost s-electrons are included as constituent elements of the oxide, because even if the crystal structure becomes amorphous, the s-orbitals of the heavy metal ions that make up the conduction band minimum (CBM) have a large spatial extent, so the effect on the overlapping areas is minimized. This is illustrated in Fig. 3.6.
- In facilitating the formation of an amorphous state, a multi-component oxide containing several metallic elements (preferably including heavy metal elements) is more preferable than a simple oxide.

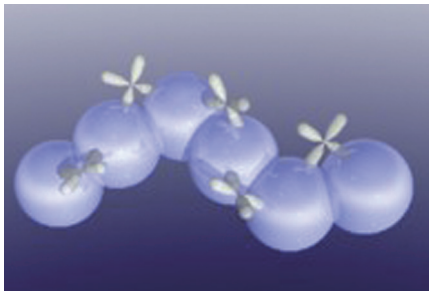

Fig. 3.6 Image of overlapping spherically symmetric s-electron orbitals of large radius.
It is inferred that even if the crystal lattice is disordered, the presence of broadened spherically symmetric s-orbitals will not significantly affect the electron mobility, since the orbital overlap will remain to some extent. (This illustration is courtesy of Prof. Hideo Hosono.)

- Metal complex oxides consisting of heavy metal cations with an electronic configuration of
  $(n-1)d^{10}ns^0$ $(n\geq4)$
  are good candidates as transparent and electrically conducting/semiconducting materials that satisfy the above conditions.

3.4 Transistor Application by Using Epitaxially-Grown Single Crystalline Homologous $InGaO_3(ZnO)_m$ Thin Films

Here, the author would like to speculate on the trends of the ERATO HOSONO project just prior to the publication of the *Science* journal and the flow of technology leading up to its publication. Two key technologies exist in the technology published in *Science*: (1) the homologous phase of the crystal: $InGaO_3(ZnO)_m$ was used as the material, and (2) the reactive solid-phase epitaxial growth method was chosen as the fabrication process. Since the latter is discussed above, I would like to discuss again the history of the homologous crystalline phase in (1), which is also discussed in Chapter 2.

Noboru Kimizuka, who was working at the National Institute for Research in Inorganic Materials at the time, established the basic materials science regarding crystalline $InGaO_3(ZnO)_m$. At least five papers[184)-188)] of his homologous oxide studies correspond to the research on the crystal structure chemistry of $InGaO_3(ZnO)_m$ crystals. Kimizuka et al. were purely engaged in materials science and identified the structure of the material, clearly showing that $InGaO_3(ZnO)_m$-based crystalline phases existed in the world, but the author can not find any results on the evaluation of electrical or optical properties in the Kimizuka's papers of the time.

On the other hand, Kunihito Koumoto of Nagoya University, who had been searching for highly dimensional materials in the development of thermoelectric conversion materials, paid attention to a series of material science research results by Kimizuka et al. and published research on thermoelectric evaluation of homologous oxides in 1996 and 1997[189), 190)]. The first author of that first paper was Hiromichi Ohta, who would join ERATO a few years later. Both reports are for polycrystalline and sputtered thin films of $In_2O_3(ZnO)_m$, which is a typical homologous phase but does not contain Ga, Koumoto investigated electric conductivity and Seebeck coefficient et al. Of course, Koumoto's papers also cite Kimizuka et al.

In March 1996, Ohta completed his master's course at Nagoya University and worked at the research institute of a private company. In January 1998, he was re-employed at HOYA Corporation's R&D Center[191)]. Later, although the reason is unclear, he engaged in joint research with Kimizuka at the National Institute for Research in Inorganic Materials and published two co-authored papers[192), 193)]. However, the topic of the joint research was on In-Fe-Ti-O multi-element oxides, all of which are similar to homologous materials and none of the materials was associated with transparent conducting materials. The author speculates that HOYA, a private company, might have hoped to leverage Kimizuka's technical expertise as a materials researcher with profound knowledge of homologous materials within the company while preventing contamination in their primary area of focus, which was transparent conducting materials. Moreover, when contemplating the flow and transition of technology, it is very interesting to note that Masahiro Orita, who joined the ERATO project from HOYA (presumably on secondment), similar to Ohta, also co-authored 2 papers on the joint research results by HOYA and Kimizuka.

And Toshihiro Moriga of the University of Tokushima visited Poppelmayer's laboratory at Northwestern University, where he collaborated with Poppelmayer, and published two papers[194), 195)] in 1998 and 1999 on the electrical conductivity and optical characterization of homologous polycrystalline oxides in terms of the development of next-generation transparent conducting materials. The 1998 paper is on the $In_2O_3(ZnO)_m$ system, and the 1999 paper is on the $InGaO_3(ZnO)_m$ system. In particular, the latter paper on $InGaO_3(ZnO)_m$ polycrystals[195)] was the first paper in the world to evaluate the electrical and optical properties of the homologous $InGaO_3(ZnO)_m$ system with $m > 1$ and is considered to have published very useful information, but this Moriga et al. paper was not cited in the *Science* paper published by Hosono et al. in 2003. Perhaps one of the reasons behind this is imagined to be the fact that this period coincided with the launch of ERATO and the enormous amount of administrative work that had to be done, including having to comply with regulations that required the establishment of a research base in a different location than the Tokyo Institute of Technology's on-campus area. In addition, because Hosono was promoting research projects on an extremely large number of material systems, including n-type and p-type oxide semiconductors, and amorphous oxide semiconductors, the author suspects that Hosono's group simply did not notice the existence of this Moriga et al. literature. More interestingly, in the references of Moriga's paper[195)], which first reported

the electrical properties of $InGaO_3(ZnO)m$ based polycrystals (m>1), the paper[196] on $InGaZnO_4$ published by Orita of HOYA as a transparent conducting oxide in 1995, is not cited. Perhaps, because the concept that $InGaZnO_4$ crystals with $YbFe_2O_4$-type crystal structures is part of a family of homologous structures had not yet taken hold, the author imagines that Orita's paper was not cited in Moriga's paper at the time. In any case, it is difficult for any researcher to cite references in a way that satisfies everyone 100%. It is believed that this has been the experience of many researchers.

When Masahiro Orita, who had joined the ERATO Hosono Project from HOYA, returned to his old position at HOYA, Kenji Nomura, a doctoral program student, newly joined the project. Nomura published a paper[66] on $In_2O_3(ZnO)_m$ single crystals in 2002 and reported[67] on the fabrication of field-effect transistors of $InGaO_3(ZnO)_5$ single-crystalline thin films in the following year, 2003. The former is an $In_2O_3(ZnO)_5(001)$ single-crystalline thin film on a YSZ(111) substrate obtained using the Reactive Solid-Phase Epitaxy Method[68), 73), 74), 76), 104], devised by Ohta from the Hosono Project. The latter was presented during an MRS meeting related to the transistor characteristics of $InGaO_3(ZnO)_5$ single-crystalline thin films, the contents of which were almost similar to those in *Science*. However, the mobility mentioned then was only 2 cm^2/Vs. One of the reasons is that an amorphous Al_2O_3 film was used as the gate insulating layer. However, in the corresponding paper[70], it was reported that as the value of m in $InGaO_3(ZnO)_m$ is increased, the mobility also increases, with field-effect mobility increasing proportionally from 1 to 10 cm^2/Vs for m = 1 to m = 10. Nomura conducted an investigation into the temperature dependence of the electron transport characteristics for $InGaO_3(ZnO)_m$ single-crystalline thin films and reported that materials become degenerate (metalize) when the carrier density is $4x10^{18}$ cm^{-3} or more, which indicates that he was making preliminary preparations for transistors[71]. He has also mentioned in his next report[72] that the mobility increases rapidly when the carrier density is $3x10^{18}$ cm^{-3} and above, and has also reported that when the gate insulator is replaced by HfO_2, which has a high dielectric constant, the mobility becomes 80 cm^2/Vs. This result is considered to be reflected in *Science*[69]. It is inferred that in addition to controlling the carrier density of the $InGaO_3(ZnO)_5$ thin film, replacing amorphous Al_2O_3 with amorphous HfO_2 for the gate insulator must have significantly contributed to the improvement of characteristics.

Here, the historical flow of materials research leading up to the contents published in *Science* in 2003 is depicted from the author's perspective on a paper-by-paper basis, as shown in Fig. 3.7.

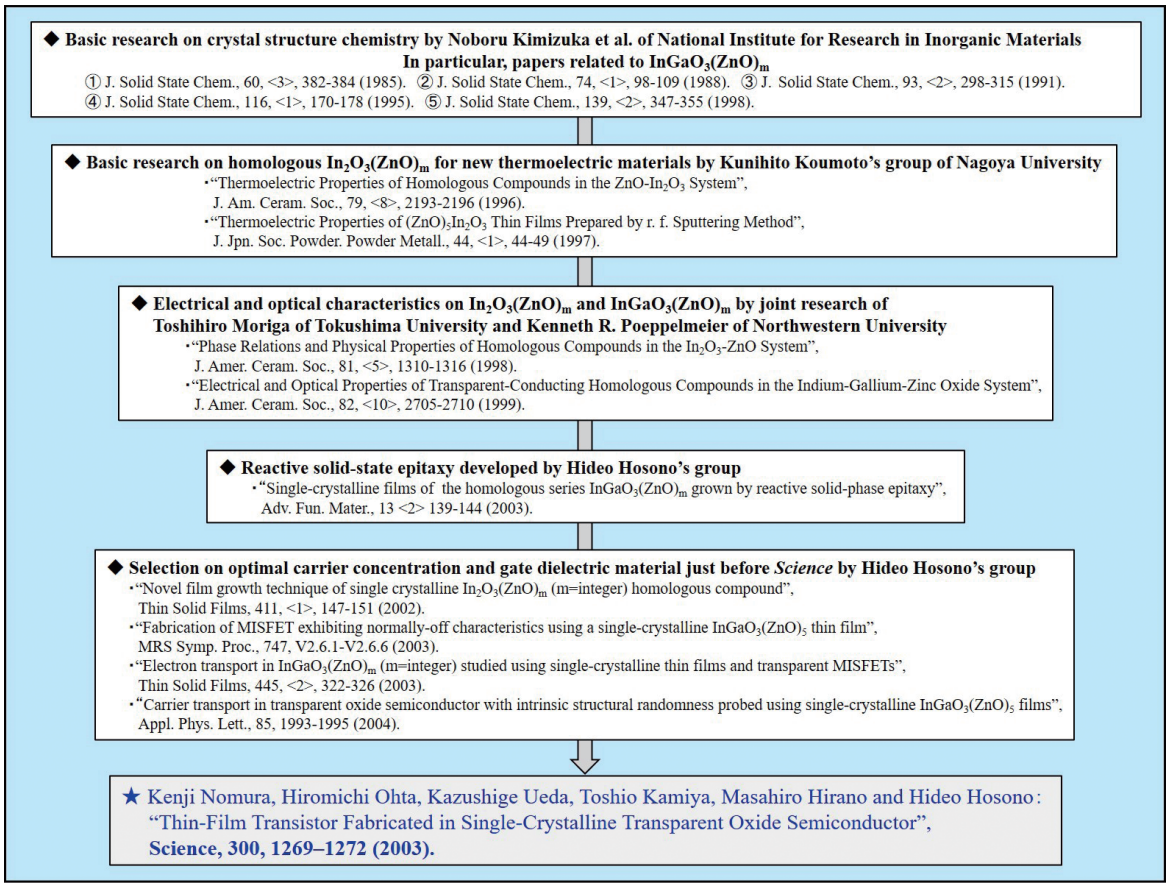

Fig. 3.7 Historical flow of materials research leading up to the publication of the Science paper: Approach to substance – material – device.

3.5 From Crystalline Conducting Oxide, $InGaZnO_4$ To Amorphous Semiconducting Oxide, a-$InGaZnO_4$

3.5.1 The Research on Crystalline Conducting Oxide is Completely Different from The Research on Amorphous Semiconducting Oxide

In this section, I want to look at the important technological developments leading up to transistors using amorphous oxide semiconductors from the author's perspective. In general, in the research and development of inorganic materials, mainly oxides, the technological development is from (1) powder, (2) polycrystals (sintered body), (3) polycrystalline thin film, (4) epitaxial single-crystalline thin film, and (5) simple device fabrication (p-n junctions, simple transistors, etc.). In some cases, the technological development may shift midway to (6) nanoparticles and even (7) quantum dots as photocatalysts or new photoelectric conversion materials. However, there is usually no "amorphous" stage in the process. In other words, until now, most researchers in the material science field worldwide have not considered amorphous materials as a strong candidate for practical electronic materials.

In stark contrast to the usual flow of technology described above, Hosono has been strategically aware of "amorphous oxides" from the early stages of his research projects. From the point of view of researchers in the same field, it is no wonder that his strategy is seen as downright "heretical". The author also highly appreciates the decisiveness and vision of Japan Science and Technology Agency (President: Moritaka Nakamura), which entrusted Hosono with the highest position as the research director for this extremely risky and difficult-to-understand research project.

The specific image of Hosono's amorphous strategy route, as mentioned above, can be considered to have been largely opened with the discovery of three amorphous oxide semiconductors: a-$AgSbO_3$[21], a-Cd_2GeO_4[17], a-Cd_2PbO_4[24]. By looking at the experimental results of these amorphous oxides, Hosono found a common design guideline for candidate materials for amorphous oxide semiconductors. This is known today as "Hosono's Working Hypothesis"[91]. The summary of this hypothesis is that metal complex oxides composed of heavy metal cations with an electron configuration satisfying the condition described in the previous section: (n-1) $d^{10}ns^0$ ($n \geq 4$) may be a good candidate for suitable amorphous oxide semiconductors.

When considering the material history of amorphous oxide semiconductors, there is an essentially significant difference between amorphous and crystalline materials, as discussed in Section 3.1.6. The author would venture to add that the physics being pursued is very different in the exploratory studies of conducting oxides and oxide semiconductors. To put it in a simple way, research on amorphous materials is completely different from research on crystals, and the author believes that the technological history of amorphous materials should be distinguished from that of crystalline materials. This time, however, there are some details that inevitably need to be conveyed, not from the perspective of material design, but from the perspective of recruiting human resources. The following is a careful explanation, including the author's reasoning and speculation.

3.5.2 Early Basic Research on $InGaZnO_4$ as a Transparent Conducting Oxide Crystal

Hosono and Kawazoe are considered to have started joint research[129] with HOYA in the mid-1990s. In 1992, Kawazoe of Tokyo Tech and Naoyuki Ueda et al. of the Institute of Molecular Science published a paper on $MgIn_2O_4$ as a new transparent conducting oxide at that time, the aim of which was probably to further lower resistance and remove Indium from ITO materials.[1] One or two years later, Tanji et al. of HOYA published a paper[197] on the same Mg-In-O. It is assumed that this connection probably led to the fostering of communication between researchers of Tokyo Tech and HOYA around 1994 under the common theme of "development of transparent conducting oxides", and the seeds of joint research were planted.

Under such circumstances, a paper on a new conducting oxide $InGaZnO_4$ was reported[196] by Masahiro Orita et al. of HOYA's R&D Center. The research motivation was probably the exploration of a new material as a substitute for ITO; however, coincidentally, this material had the same composition as the channel layer, $InGaZnO_4$ of the amorphous IGZO-TFT, later published in *Nature*. This material was polycrystalline (sinter body), and the main focus of HOYA's research and development was to develop a material that is transparent in visible light and highly conductive. It was completely different from amorphous oxide semiconductors. However, the material had the same composition, and the paper's first author was Masahiro Orita, who joined the ERATO "HOSONO Transparent ElectroActive Materials Project" a few years later. For this reason, we have to touch upon Masahiro Orita's work, starting from the research outcomes during his time at HOYA to his research around the time he participated in the ERATO Project. Even though joint research had been initiated between HOYA and Tokyo Tech, it remains uncertain whether the contents of this JJAP paper[196] by Orita were discussed during the regular meetings of both parties throughout the joint research since there is a boundary regarding what a company is permitted to disclose. However, at least Hosono must have certainly understood the qualities of the material. At the time when Orita published his paper, they were probably still working toward the same goal (transparency and improved conductivity). From here on, although it is only the author's speculation, after ERATO was launched around the year 2000, Hosono must have thought, "I would like to try amorphous materials someday", and must have begun to envision such a story in his mind that "If the material is amorphous, unlike crystals, the triangular phase diagram of $InO_{1.5}$-$GaO_{1.5}$-ZnO can be infinitely adjusted, and in the process, unlike simply having high conductivity, it may be possible to find a material with a suitable carrier concentration that will eventually

achieve the normally-off function when used for transistors".

The JJAP paper[196] published by Orita of HOYA suggests that $InGaMgO_4$ and $InGaZnO_4$ would be candidates for transparent conducting oxides. In particular, the latter, $InGaZnO_4$, is reported to be a good conductive material with a mobility of 20 cm^2/Vs and a carrier density of 4 x $10^{19}/cm^3$. The papers referred to by Orita's group in this paper are the considerations on transparent conducting oxides [$CdSnO_3$, Cd_2SnO_4, In_2TeO_6, $CdIn_2O_4$, etc.] from the viewpoint of crystal chemistry[198], published by Shannon et al. of DuPont in 1977, the paper[199] on the introduction of oxygen defects and the efficacy of Ge doping to Ga sites and Sn doping to In sites in the transparent conducting oxide $GaInO_3$ published by Cava, etc., of AT&T Bell Laboratories, and a series of research results on many transparent conducting materials, including $MgIn_2O_4$[1], $CdGa_2O_4$[12], $ZnGa_2O_4$[13], and $Cd_2Sb_2O_7$[16] by Kawazoe and Hosono's group at Tokyo Tech. By referring to the literature of their predecessors, Orita's group focused on 4 polycrystals (ceramics) [= $InGaMgO_4$, $InAlMgO_4$, $InGaZnO_4$, and $InAlZnO_4$] with $YbFe_2O_4$-type crystal structure (layered structure), evaluated their basic optical and electrical properties, and identified 2 oxides shown in Table 3.5 as promising candidates for transparent conducting materials.

The research in Orita's paper is intended for use as transparent electrodes, and the mobility measurements in this study were carried out using unoriented samples. Therefore, his paper notes that there is room to greatly improve conductivity by orienting the c-axis of the layered $InGaZnO_4$ crystals. Orita also mentioned two specific material design methods for improving carrier density by one order of magnitude: the introduction of oxygen defects and doping with higher valence ions of metals. He cites the results of the collaboration[200] between Yuzo Shigesato of Asahi Glass Co., Ltd. and David C. Paine of Brown University, and mentions that Sn doping in ITO can inversely lower the electron mobility in some cases. Simple doping operations may cause electron scattering due to lattice distortion. For this reason, Orita carefully discusses the need to improve the conductivity of layered $InGaZnO_4$ materials by doping carriers in the $GaZnO_{5/2}$ layer and not doping carriers in the $InO_{3/2}$ layer, which is thought to be the electron pathway for the purpose of preventing electron scattering. This attitude of Orita toward material exploration is indeed a good argument and it is thought that the attitude is very legitimate. Hosono must have seen more than simply putting the potential of the material $InGaZnO_4$ into memory; he must have seen the high quality of Orita, the author of this paper, as a materials researcher. The author is convinced of this.

Table 3.5 Electrical and optical characteristics for $InGaMgO_4$ and $InGaZnO_4$, which are both candidates in novel conducting oxides[196].

Candidate oxides	Optical band gap [eV]	Electron mobility [cm^2/Vs]	Carrier density [cm^{-3}]
$InGaMgO_4$	**4.2**	**～ 2**	**～ 1 x 10^{18}**
$InGaZnO_4$	**3.5**	**～ 20**	**～ 4 x 10^{19}**

The following year, in 1996, Orita et al. of HOYA collaborated with the National Institute of Materials and Chemical Research (one of the predecessors of AIST) to evaluate the electronic properties of crystalline $InGaZnO_4$ thin films by sputtering[201]. In this paper, it was reported that by increasing the annealing temperature in a hydrogen (reducing) atmosphere, both the electron mobility and the carrier concentration increase, and by annealing at 600ºC, the carrier concentration reaches $1x10^{20}/cm^3$ and the electron mobility μ reaches 24 cm^2/Vs. In addition, he also indicated that the InO layer is important for the electrical conduction path. Later, Orita also collaborated with the Computational Science Group at Kyoto University on this conduction mechanism. They concluded that the CBM in the band structure is due to the overlap of the 5s-orbitals of In in the InO_2 layer derived from the crystal structure, and high electrical conductivity of the entire system can be expected by adding dopants to the $GaZnO_2$ layer[202].

From the several papers by Orita et al. of HOYA mentioned above, the author infers that Hosono felt that $InGaZnO_4$ could be a promising candidate material for transistor applications, which had been difficult with conventional ITO. At the same time, Hosono must have strongly wanted to bring Orita of HOYA, who had been collaborating with several research institutes, into the new ERATO project that was about to begin. In designing materials for Hosono's transistors, it is sufficient to have a certain carrier density, while maintaining high mobility. In addition, it is thought that Hosono has firmly drawn out in his original design concept that the material design using an amorphous phase, which may easily enable suitable carrier doping and carrier control by fine-tuning the In/Ga/Zn metal element ratio, would demonstrate a wider range of capabilities. The three elemental ions, trivalent In^{3+} and Ga^{3+} and divalent Zn^{2+}, all satisfy the candidate condition $(n-1)d^{10}ns^0$ ($n \geq 4$). The condition-satisfying status of these three elements may be coincidental, but it is certainly very attractive for material exploration.

Hosono's material design concept for this $InGaZnO_4$ must have been to make it amorphous, adjust the carriers in a rather suppressive direction, and check the semiconductor characteristics by making a simple transistor device. If so, the author believes that the idea of carrier doping by fine-tuning the metal element ratio of In/Ga/Zn is a very outstanding material design concept that has rarely been considered in the materials science of multi-component oxides.

3.5.3 A Great Switch in Material Design Policy to Amorphous a-$InGaZnO_4$

The early significant research outcome by Masahiro Orita, who had joined the ERATO "HOSONO Transparent ElectroActive Materials Project", was the one he presented at the MRS Spring Symposium held at San Fransisco, USA, in April 2000[79]. The author believes that a research presentation "U5.23 'Properties of a Novel Amorphous transparent conducting oxide, $InGaO_3(ZnO)_m$'" from Orita, a new member of the ERATO Hosono Project, at the "Symposium U—Materi-

als Science of Novel Oxide-Based Electronics" session at this international conference, was an important starting point that led directly to the publication in *Nature* in 2004.

Among the presenters' names was Hiromichi Ohta, who had joined ERATO from HOYA at the same time, and Kawazoe, listed as affiliated with HOYA's R&D Center, who had retired from Tokyo Tech. This was very interesting in terms of the composition of the presenters. The composition with m = 1 of $InGaO_3(ZnO)_m$ was determined to be the material most likely to be in the amorphous phase, because the X-ray diffraction peak occurs at $m \geq 5$ and the material becomes crystalline, while at $m \leq 4$, the material shows a halo in the form of X-ray diffraction, and the Selected Area Electron Diffraction (SAED) pattern of Transmission Electron Microscope (TEM) shows a diffuse ring pattern only at m = 1. The optical transmission spectra showed that the optical band gap (sometimes called Tauc Gap because of the value obtained from a Tauc Plot) and the visible transmission wavelength range increases as the m-value changes from 4 to 1. The mobility is relatively high compared to other values of m, even at low carrier density, as shown in Table 3.6. It is considered that a very high mobility is maintained for a highly amorphous material.

On the other hand, regarding temperature dependence of the electrical conductivity, since there is hardly any temperature dependence, thin films with any value of m are considered to be degenerate semiconductor-like (metallic-like behavior). As the title of this presentation suggests, the material is treated as a conductive oxide and is not described as a semiconductor. Therefore, the normally-off condition of semiconductor transistors cannot be achieved in this state. Hence, Hosono must have considered that it would be necessary to reduce the carrier concentration by several orders of magnitude eventually. The following year, Orita of ERATO published a paper with similar content, in which the electrical conduction mechanism was discussed, and it was suggested that the 4s orbital of Zn plays an important role therein[80]. In the MRS symposium mentioned above, it was recognized that the contribution of Zn^{2+} is larger than that of In^{3+} in the conduction mechanism, considering Slater's rules on ionic radii, etc. However, in this paper[80], the last section of the abstract states that "The present system is the first amorphous oxide semiconductor in which Zn 4s orbitals form the extended conduction band" and concludes that this is the first report on an amorphous oxide semiconductor in which the 4s orbital of Zn plays a major role in the electrical conduction.

As described in Chapter 5 below, for Masahiro Orita who had been exploring new conductive oxides using crystals while working at HOYA, Hideo Hosono, a project leader, made the bold and wise decision to take the plunge and switch not only using a crystal phase to using an amorphous phase but also design to conductors with high carrier density to semiconductors with controlled carrier, under the new guideline for JST's project organization called "Transparent Electro-Active" which gives an image of diverse physical property functions. When Orita was briefed on this new research concept, the author suspects that he was at a bit of a loss as to how the experience he had accumulated along the lines of crystallography and epitaxial growth, plus conductivity enhancement, could be utilized in future project themes. On the other hand, the author imagines that Hosono, who explained the research concept of the newly established ERATO project, would have explained it very carefully to Orita and Ohta, the main members of the project, so that they would fully understand the importance of the development of semiconducting materials and its significance. For both parties, this must have been a very big hurdle and decision to make so soon after the start of the ERATO project.

I will now briefly touch upon the electrical conduction mechanism. In Orita's papers[196), 201), 202)] during his time at HOYA, the $5s^0$ orbital of In^{3+} was considered to have been playing the main part in the electrical conduction of crystalline $InGaZnO_4$; however, in Orita's two papers[79), 80)] on amorphous $InGaZnO_4$ after he participated in ERATO, it is stated that the $4s^0$ orbital of Zn^{2+} is mainly responsible. Since crystals have a periodic structure, it is not surprising to note that amorphous materials, which do not have a periodic structure, have a different electrical conduction mechanism. For those, including the author, who lack experience beyond experimental research, the type of orbital of the elemental ion contributing to the lower end of the conduction band is of little concern because, whether it's In^{3+}, Zn^{2+}, or Ga^{3+}, ions of any element in any of these 3 metal cations meet the conditions of "Hosono's Working Hypothesis". However, from the perspective of materials science and solid-state physics, there is no doubt that discussing the main carrier of electrical conduction is extremely important scientifically.

Subsequently, in 2007, Nomura et al. of Hosono's group again conducted a detailed analysis of electron carriers at the

Table 3.6 Optical and electric characteristics in amorphous $InGaO_3(ZnO)_m$ thin films with various m value[79)].

Composition and m-value of sputtering targets	Tauc Gap [eV]	Average Transmittance (%)	Carrier density [$10^{20}cm^{-3}$]	Electron mobility [cm^2/Vs]	Electric conductivity [S/cm]
1 [= $InGaZnO_4$]	3.00	81	0.77	20.8	256
2 [= $InGaO_3(ZnO)_2$]	2.95	85	1.37	12.8	281
3 [= $InGaO_3(ZnO)_3$]	2.95	81	0.60	17.7	171
4 [= $InGaO_3(ZnO)_4$]	2.85	79	1.22	20.9	408

lower end of the conduction band using Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) and *ab-initio* calculations and reported[87] that even in amorphous materials, $5S^0$ of In^{3+} plays the main part in the electrical conduction, which is the same as in crystals, due to the residual orderliness of structure in short-range spaces, etc. This issue related to the electrical conduction mechanism has seemingly provided a significant motivation to researchers around the world and Prof. J. E. Medvedeva et al. of Missouri University of Science and Technology, USA, whose primary field of research is the computational science of transparent conducting oxides, have continued to actively report on the conduction carriers in transparent conducting oxides or transparent oxide semiconductors since around 2007 to date[203)-208)]. Although we leave the details to the original papers, it is interesting to note that $InGaZnO_4$ enters a degenerate state as soon as carriers are introduced. There is also an interesting mention[204)] of the conduction mechanism in which the electron transport in the conduction band is assumed to be due to contributions from both the $InO_{1.5}$ layer and $GaZnO_{2.5}$ layer. Since this issue essentially has a lot to do with the structural state of amorphous materials, we look forward to the development of continued analytical research.

3.5.4 Change of Material Design toward Controlling Carrier Concentration of Amorphous a-InGaZnO$_4$

Returning to the original topic, amorphous $InGaZnO_4$ later appeared in the paper in the context of fabricating an all-amorphous p-n junction[62)]. As described in detail in the previous section, a-$InGaZnO_4$ thin film (E_g = 3.0 eV) deposited at room temperature had an electrical conductivity of $1.4x10^{-1}$ S/cm, a carrier density of $4.2x10^{16}cm^{-3}$, and a mobility of 21 cm^2/Vs. The point to note here is the carrier density. In the previous two reports[79), 80)], the carrier density was $0.77x10^{20}$ cm^{-3} in both cases, and the material entered a degenerate state due to the temperature dependence of the electrical conductivity. In other words, when Narushima fabricated an all-amorphous p-n junction, the carrier density of the a-$InGaZnO_4$ phase decreased significantly by about 3 orders of magnitude. Later, although Toshio Kamiya in Hosono's laboratory explained[209)] that the optimal conditions for transistor operation (without heat treatment) were a carrier density of $10^{12} \sim 10^{15}cm^{-3}$ and an electrical conductivity of $10^{-6} \sim 10^{-3}$ S/cm, I imagine that the adjusting conditions for amorphous $InGaZnO_4$ thin films (oxygen partial pressure control during deposition) were being developed in the form of recipes for each application in Hosono's laboratory at that time. A carrier density of around 10^{16} cm^{-3} would probably have been sufficient for a p-n junction element. In fact, according to the paper published in *Nature*[81)] in 2004, in which the electrical conductivity of amorphous a-$InGaZnO_4$ phase is adjusted below 10^{-5} S/cm and the carrier density is adjusted below 10^{14} cm^{-3}, this suppression of the carrier density was clearly a required specification for the channel layer to reduce the off-current and obtain a sufficient on-off ratio. Paradoxically, the oxide a-$InGaZnO_4$ was outstanding in its ability to adjust its carrier concentration over an extremely wide dynamic range. The discovery of this amorphous a-$InGaZnO_4$ was made possible by Hosono, who was the leader, and also by the continuous efforts of many members of the ERATO project at that time, including Masahiro Orita, Kenji Nomura, Hiromichi Ohta, and Toshio Kamiya, who were all enthusiastic about materials science.

In this way, the Hosono Project established a process that can sufficiently avoid a degenerate state in electrical conduction by adjusting the carrier concentration in the a-$InGaZnO_4$ thin film and is thus thought to have steadily climbed the stairs toward its original purpose as a channel layer for thin film transistors. The historical development of material technology leading up to the contents published in *Nature* in 2004, which will be discussed in Chapters 4 and 5, can be illustrated from the author's perspective on a paper-by-paper basis, as shown in Fig. 3.8.

The details and significance of the contents published in *Nature* in 2004 are described in Chapter 5. However, in a sense, it was completing the homework I had given myself at the International Conference on Amorphous Semiconductors[91)] in 1995. In 2005, 10 years after the International Conference on Amorphous Semiconductors, which had generated little interest, Hosono must have been delighted when he received an invitation to give a keynote speech at the 21st International Conference on Amorphous and Nanocrystalline Semiconductors (ICANS) in Lisbon, Portugal. The first words of Hosono in his keynote speech were, "This presentation is a kind of revenge"[210), 211)]. It is believed that these first words were spoken, looking back over the past 10 years, filled with various thoughts and feelings. The contents of this lecture were published in the 2006 issue of *the Journal of Non-Crystalline Solids*[110)] and in addition to 2 triangular phase diagrams of In_2O_3-Ga_2O_3-ZnO that were not included in *Nature* (crystal and amorphous phase diagrams and electronic phase diagrams of carrier density and electron mobility obtained from Hall measurement), several physical property measurements of amorphous a-$InGaZnO_4$ were disclosed, including an important correlation diagram between oxygen partial pressure and carrier concentration during deposition, a relationship diagram of carrier density and Hall mobility, and a diagram of the temperature dependence of Hall mobility. The triangular phase diagram of In_2O_3-Ga_2O_3-ZnO is shown in Chapter 5, while the other 3 diagrams are shown in Fig. 3.9 (a), (b), and (c), respectively.

The characteristic of this amorphous a-$InGaZnO_4$ material is that, as shown in Fig. 3.9 (a), the carrier density can be controlled by at least 5 orders of magnitude by adjusting the oxygen partial pressure during deposition, and as shown in Fig. 3.9 (b), the Hall mobility also increases with the increase in the carrier density. The details of the characteristics evaluation have also been reported by Takagi et al.[82)] of Hosono's group. This behavior is similar to that of the crystalline ho-

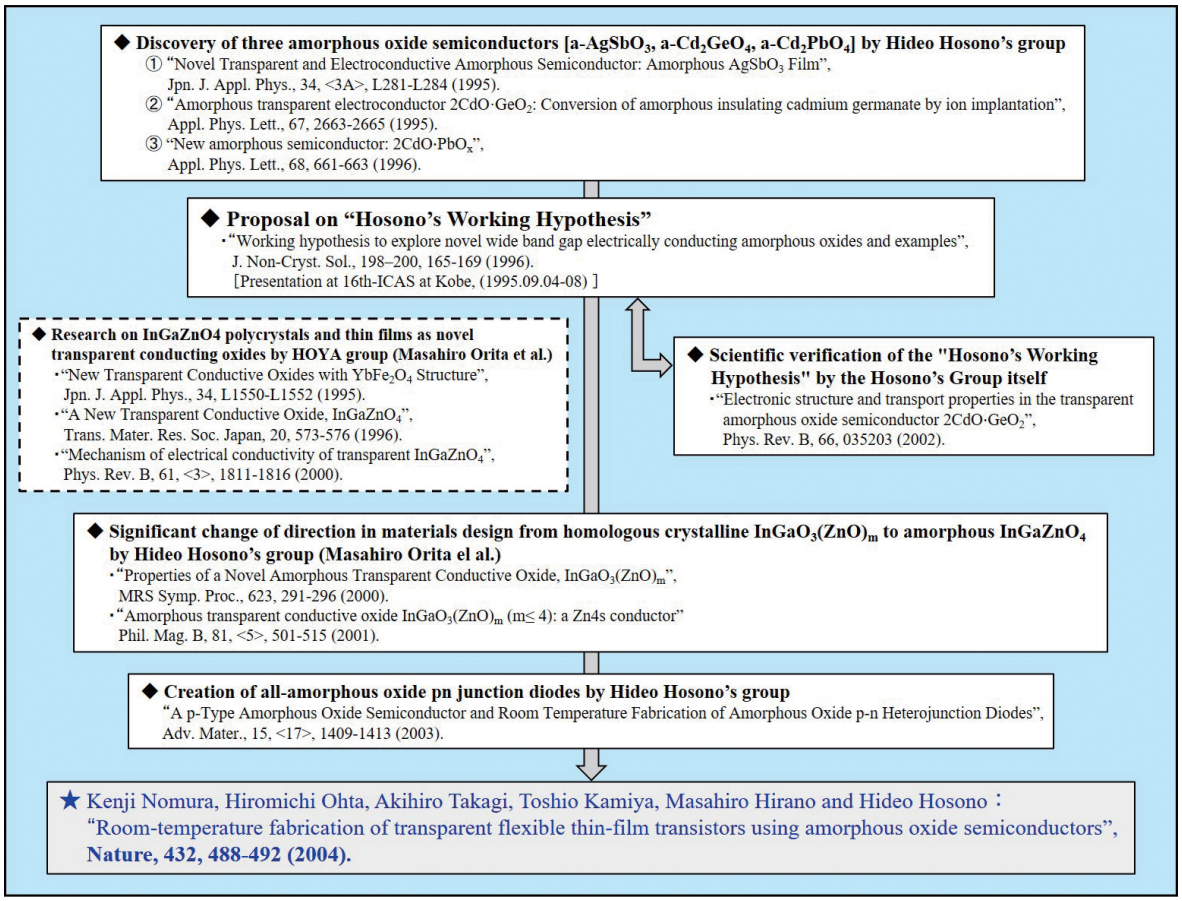

Fig. 3.8 Historical flow of materials research leading up to the publication of the *Nature* paper: Approach to substance – material – device.

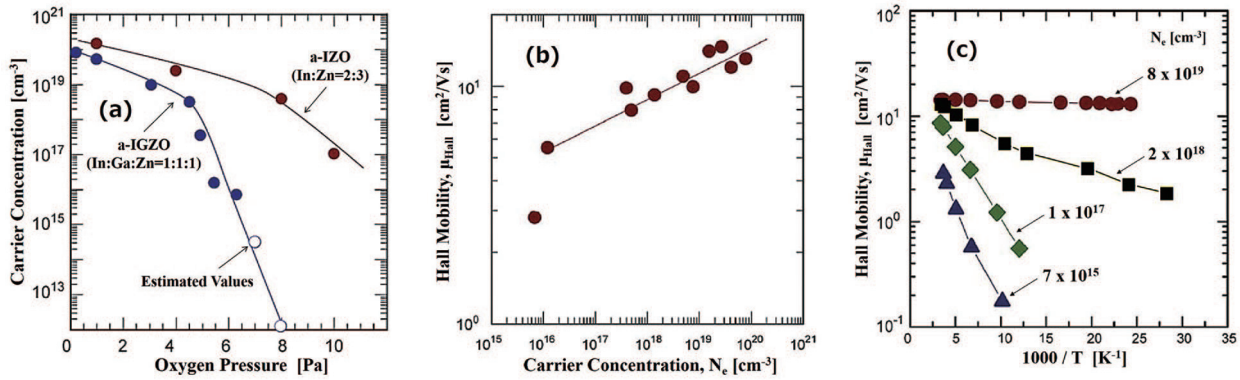

Fig. 3.9 Main electronic characteristics of a-InGaZnO$_4$ thin film.
(a) Relationship between oxygen pressure and carrier concentration. (b) Relationship between carrier concentration and Hall mobility. (c) Temperature dependence of Hall mobility with various carrier concentrations of a-InGaZnO$_4$.(Published three figures in reference (110) revised a little by courtesy of Prof. Hideo Hosono.)

mologous $InGaO_3(ZnO)_m$ oxide semiconductor[71]. However, the behavior differs from that of the Sn-doped ITO, which may have characteristics derived from the layered structure with dimensionality. Furthermore, as can be seen in Fig. 3.9 (c), the different temperature-dependent activation energies at different carrier densities are presumed to be due to the close linkage between carrier density and the number of oxygen defects and the existence of different potential barriers for electrical conduction in amorphous states with various oxygen contents. This material is interesting as it immediately degenerates when the carrier density is adjusted above $4x10^{18}$ cm^{-3}.

Most of the functional oxide thin films by Hosono's group introduced in this chapter were fabricated by the pulsed laser deposition (PLD) method. The PLD system is a thin film fabrication tool[212)-214)] developed and advanced by Prof. Hideomi Koinuma and Assistant Professor Masashi Kawasaki at Tokyo Tech. It is a powerful tool for combinatorial technology in materials exploration. The greatest outcome of this film deposi-

tion tool is probably the "IGZO-TFT" produced by Hosono of Tokyo Tech. In other words, this PLD system is also important from a historical perspective because it produced a-IGZO, an amorphous oxide semiconductor of industrial importance, which can be an alternative to amorphous silicon. A photo of the PLD system is shown in Fig. 3.10. In particular, some of the PLD systems used in Hosono's laboratory can control the substrate temperature up to an ultra-high temperature of 1500°C and the oxygen partial pressure in the chamber over a wide range of 100 Pa to $5x10^{-6}$ Pa, and all of the systems are very attractive tools for material creation, with many having special specifications that allow for exploratory creation of materials, from amorphous thin films of oxide semiconductors to epitaxial single-crystalline thin films[99].

In these three chapters, I have described the research and development by Hosono's group on transparent oxide semiconductor materials from the early 1990s to the publication in Nature in 2004, also considering the author's reasoning and imagination. To conclude this chapter, I would like to tell you about the events leading to the ERATO "HOSONO Transparent ElectroActive Materials Project" launch in October 1999. A description of Hosono's work and his feelings at the time of his appointment as research director can be found in the 2014 *Journal of the Japan Society for Precision Engineering*[215]. This document[215] is very valuable for understanding the situation at the time of the project's launch, which describes how ERATO had an assured budget of 1.5 billion yen at that time to cover the research expenses over 5 years. However, everything, including the research location, the team organization, and the hiring and treatment of the researchers, needed to be decided, and how the ERATO project was started with a research base at the Kanagawa Science Park (KSP) rather than at Tokyo Tech, because back then, research was conducted off-campus, in principle.

In addition, there are many papers and reviews, including the 3 reviews[216)-218)] in OYO-BUTURI (the Journal of the Japan Society of Applied Physics), which explain the materials technology in detail while taking an overview of the new oxide semiconductor research since 1992 to transparent amorphous oxide semiconductor transistors, and Monthly OPTRONICS[219)], Monthly Function & Materials[220)], which accurately compile the research results of the ERATO project, and Kotai Butsuri (SOLID STATE PHYSICS) published by AGNE Gijutsu Center[221)], among many others, each one of which is undoubtedly very useful in understanding the development of materials technology and the essential properties of materials. There is a possibility that an erroneous understanding has been conveyed in this survey report due to the author's limited knowledge. For a correct understanding, it would be appreciated if you could refer to the many review papers[222)-236)] by Hideo Hosono, Toshio Kamiya, Kenji Nomura, Masahiro Hirano, and others, and other references.

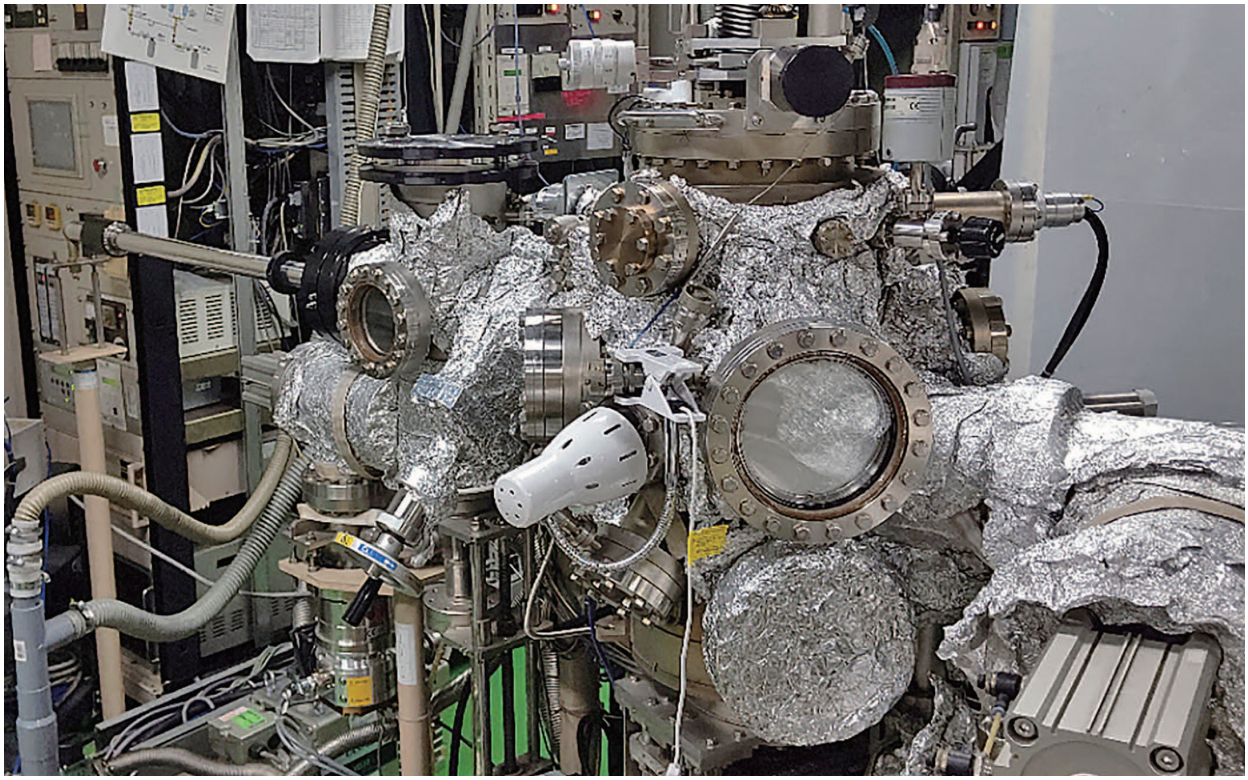

Fig. 3.10 Pulsed laser deposition (PLD) system creating novel transparent amorphous oxide semiconductor, "a-IGZO" in Hosono's laboratory.
(This photograph is courtesy by Prof. Hideo Hosono.)

Column: Comparison of Electrical Conductivity of Various Materials

For reference, the positioning of amorphous a-$InGaZnO_4$ concerning electrical conductivity is shown in Fig. 3.11, along with other metals, semiconductor materials, or insulating materials.

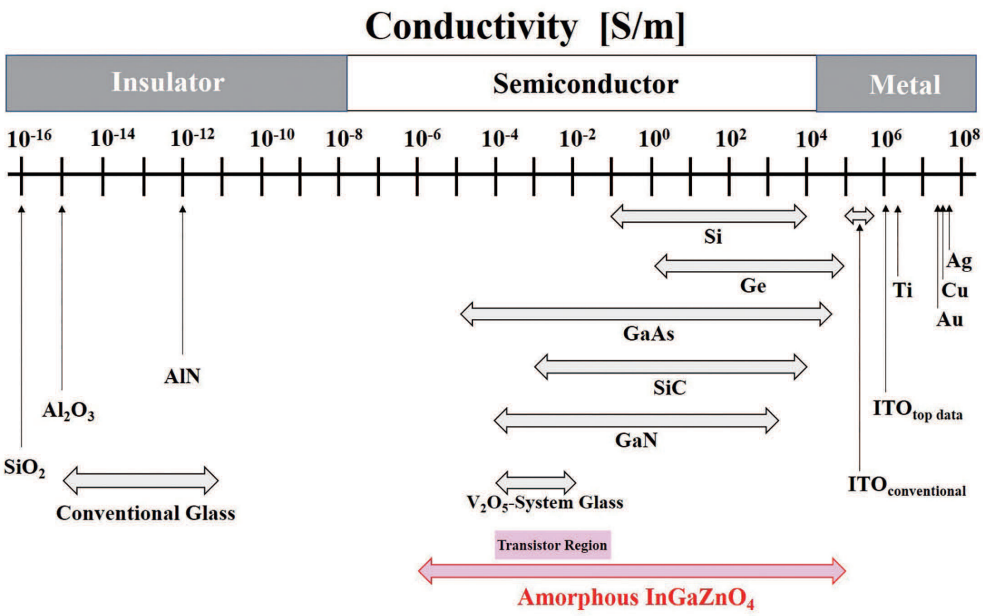

Fig. 3.11 Electric conductivity of various materials

Amorphous a-$InGaZnO_4$ is a unique semiconducting oxide material, the electrical conductivity of which can be varied over a wide range from a semi-insulating state to a degenerate semiconducting state close to metallic conduction, depending on how it is adjusted. According to Kamiya, transistors with good TFT characteristics can be obtained even without heat treatment if the film is fabricated under deposition conditions, resulting in an electrical conductivity of $10^{-4} \sim 10^{-1}$ S/m when deposited. Though this is the author's intuition, the impression is that the ability to adjust over a wide range from semi-insulating to degenerate semiconductor (metallic) has a lot to do with the fact that amorphous IGZO-TFTs have very low off-current characteristics while also having high electron mobility.

It should be noted that the materials of interest in Fig. 3.11 are described with reference to the following references and source data. In many of the references, the unit of electrical conductivity is conventionally mentioned as [S/cm], but in this figure, the electrical conductivity is expressed in [S/m] in the SI unit system.

- Si, Ge, GaAs, SiC, GaN, AlN:
  The electrical conductivity from non-doped semi-insulating wafers to doped semiconductor wafers was used as a reference from the specifications on the website of a semiconductor single-crystal wafer distributor.
- V_2O_5-System Glass: Data from reference (143) in the main text was used as reference.
- $ITO_{top\ data}$: Data from reference (47) in the main text was used as reference.
- $ITO_{conventional}$: Based on the description in Reference [Osamu Takai: "Introduction to Transparent Conducting Films", J. Surf. Finish. Soc. Jpn., 43, <2>, 74-81 (1992).]
- Amorphous $InGaZnO_4$:
  Data from references (209) and (83), and the reference [Tzu-Chi Chou et al., "Effect of Oxygen Amount on Electrical and Transparency Characteristics of Amorphous IGZO Thin Film Fabricated by Sputtering", Trans. Mat. Res. Soc. Japan, 38, <4>, 593-596 (2013).] in the text was used as a reference.

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224) Kenji Nomura, Toshio Kamiya and Hideo Hosono: "Exploratory Research for amorphous oxide semiconductor materials to realize high-performance flexible TFTs and characteristics of flexible TFTs", Journal of the Japan Society of Polymer Processing (Seikei-Kakou), 17, <9>, 588-592 (2005). [in Japanese]
225) Toshio Kamiya, Kenji Nomura, Hideo Hosono and Hideya Kumomi: "Design of amorphous oxide semiconductors and room temperature fabrication of high performance flexible thin film transistors", The Special Prize Paper at the 19th (2005) "Advanced Technology Award," (sponsored by Sankei Shimbun Co., Ltd.)
http://www.sankei-award.jp/sentan/jusyou/2005/index.html [in Japanese]
http://www.sankei-award.jp/sentan/jusyou/2005/toko_canon.pdf [in Japanese]
(Viewed on 08.05.2022)
226) Toshio Kamiya, Kenji Nomura and Hideo Hosono: "Origins of High Mobility and Low Operation Voltage of Amorphous Oxide TFTs: Electronic Structure, Electron Transport, Defects and Doping", J. Display Technol., 5, <7>, 273-288 (2009).
227) Toshio Kamiya, Kenji Nomura and Hideo Hosono: "Present status of amorphous In-Ga-Zn-O thin-film transistors", Sci. Technol. Adv. Mater., 11, 044305 (2010).
228) Yoshiyuki Matsuo: Interview Article with Professor Hideo Hosono, "Research Methods of Dr. Hideo Hosono" Journal of Industry-Academia-Government Collaboration, Vol.9, No.9, 4-21 (2013).
https://www.jst.go.jp/tt/journal/journal_contents/before2015/pdf/2013/1309-all.pdf [in Japanese]
(Viewed on 08.06.2022)
229) Hideo Hosono: "Transparent Amorphous Oxide Semiconductors: Material Design and Application", CHEMISTRY & EDUCATION, 63, <1>, 4-7 (2015). [in Japanese]
230) Toshio Kamiya: "Design of functional compounds: From an intuitive understanding of the electronic structure of ionic solids to the practical application of amorphous oxide transistors", Kinzoku Mat. Sci. Technol., 90, <10>, 846-854 (2020). [in Japanese]
231) Masahiro Hirano and Hideo Hosono: "Exploration of Novel Functions in Transparent Oxides Based on Built-in Nanostructures", J. Cryst. Soc. Jpn., 46, 48-52 (2004). [in Japanese]
232) Hideo Hosono: "Elucidation of Characteristic Electronic Transport Properties in Transparent Conductive Amorphous Oxides", Research project in review, Nissan Science Foundation, 24, 21-24 (2001). [in Japanese]
233) Hideo Hosono: "Oxide Semiconductors: General Remarks", The Journal of the Institute of Electronics, Information and

Communication Engineers (J. IEICE), 97, <3>, 178-186 (2014). [in Japanese]
234) Hideo Hosono: "Exploring Electro-active Functionality sof Transparent Oxide Materials", Jpn. J. Appl. Phys., 52, 090001 (2013).
235) ERATO "HOSONO Transparent ElectroActive Materials" Project Research Results
Research Director: Dr. Hideo Hosono (Professor, Materials and Structures Laboratory, Tokyo Institute of Technology)
(Research Term: Oct. 1999 ~ Sep. 2004)
https://www.jst.go.jp/erato/research_area/completed/htd_pj/results_1999-2004_hosono.pdf [in Japanese]
(Viewed on 10.03.2022)
236) Detailed information related to the research results of Hideo Hosono's JST project can be found in the following descriptions.
• ERATO "HOSONO Transparent ElectroActive Materials" Project
Research Director: Dr. Hideo Hosono (Professor, Materials and Structures Laboratory, Tokyo Institute of Technology)
Research Term: Oct. 1999 ~ Sep. 2004
https://www.jst.go.jp/erato/research_area/completed/htd_PJ.html [in Japanese]
https://www.jst.go.jp/erato/en/research_area/completed/htd_P.html [in English]
(Viewed on 10.05.2022)
• ERATO "HOSONO Transparent ElectroActive Materials" Project Research Completion Report (JST Project Database)
https://projectdb.jst.go.jp/file/JST-PROJECT-7700000065/JST_1113100_7700000065_2004_%E7%B4%B0%E9%87%8E_PER.pdf [in Japanese]
(Viewed on 10.05.2022)
• ERATO "HOSONO Transparent ElectroActive Materials" Project Research Results
https://www.jst.go.jp/erato/research_area/completed/htd_pj/results_1999-2004_hosono.pdf [in Japanese]
(Viewed on 10.05.2022)
• List of academic papers, reviews, presentations, etc. of ERATO "HOSONO Transparent ElectroActive Materials" Project (as of September 30, 2004)
https://www.jst.go.jp/erato/research_area/completed/htd_pj/publications_1999-2004_hosono.pdf
(Viewed on 10.05.2022)
• Japan Science and Technology Agency (JST) Strategic Basic Research Programs ERATO "HOSONO Transparent Electro-Active Materials" Project (1999-2004)
Survey report on research development several years after project completion:
https://www.jst.go.jp/erato/evaluation/follow/follow1999_hosono_shiryo.pdf [in Japanese]
(Viewed on 10.05.2022)
• Japan Science and Technology Agency (JST) Strategic Basic Research Programs
Solution-Oriented Research for Science and Technology (ERATO-SORST) ERATO-SORST "Function Cultivation of Transparent Oxides Utilizing Nano-Structure and Their Application"
Project Research Completion Report
Research Term: Oct.1 2004 ~ Mar.31 2010
Principal Investigator: Dr. Hideo Hosono (Professor, Materials and Structures Laboratory, Tokyo Institute of Technology)
https://www.jst.go.jp/kisoken/archives/sorst/pdf/h21_hosono.pdf [in Japanese]
(Viewed on 10.05.2022)

4 History of Semiconductor Transistors

When narrating the historical changes of transistors using oxide semiconductors, it will inevitably intermingle with the history of silicon and germanium semiconductor transistors, which were the original mainstream. Chalcogenide substances such as sulfides and selenides and oxides such as CdO and Cu_2O have been the subject of research as major substances with semiconductor characteristics from earlier than silicon and germanium.

A thin-film transistor (TFT) is a three-terminal device based on the same concept of a field-effect transistor (FET) made thinner by a process that fabricates a semiconductor film on a substrate such as glass. The person who first invented the fundamental concept of the FET was Julius Edgar Lilienfeld[1], a physicist of the Austro-Hungarian Empire, shown in Fig. 4.1.

Fig. 4.1 Julius Edgar Lilienfeld.
(Source: Wikimedia Commons1))

The specification states that the device has 3 electrodes and uses copper sulfide as a semiconductor. The first patent[2] was filed in the United States in October 1926 and registered in January 1930. The image of a typical device is shown in Fig. 4.2. The second patent[3] was filed in March 1928 and registered in March 1933. The image of a typical device is shown in Fig. 4.3.

Shortly after this period, Oskar Heil[4] from Germany invented a device in which electrodes were placed at both ends of a semiconductor material, and a control electrode was placed in close proximity, leaving a gap without touching the top surface of the semiconductor, the resistance of the semiconductor was changed by changing the potential of this electrode, and an amplified signal was extracted to an external circuit. He applied for a patent in the UK in March 1935 and registered the patent in December 1935. (See Fig. 4.4) This invention can be said to be the origin of MIS-FET of today[5].

The patent specification filed by Heil mentioned for the first time the use of materials such as tellurium (Te), iodine (I), cuprous oxide (Cu_2O), and vanadium pentoxide (V_2O_5) as semiconductors. This patent is considered the first to describe the use of oxide semiconductors as transistor channels.

Thus, research in the early days of semiconductors before the year 1940 was mainly focused on chalcogen compounds and metal suboxides such as Cu_2S, Cu_2O, V_2O_5, and Se, rather than today's silicon (Si) or compound semiconductors (GaAs-based) and interest was focused on the research on conductivity due to non-stoichiometry, that is, deviations from the stoichiometric composition. The reason why the above-mentioned invention of Lilienfeld and Heil was not directly demonstrated was considered to be due to the difficulty at that time in handling the electronic states of the topmost surfaces in such material systems.

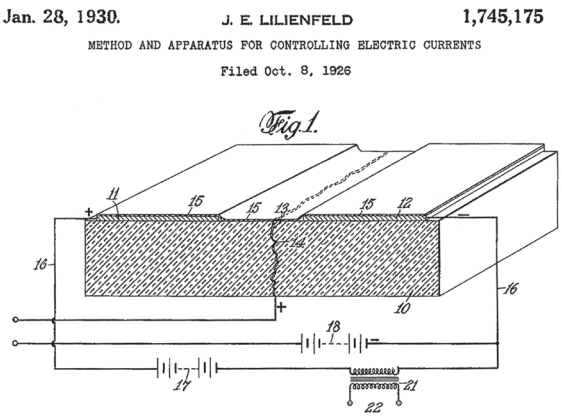


Fig. 4.2 Key component image (I) of the patent that laid the foundation for today's FET.
(Reprinted from U.S. Patent 1745175[2].)

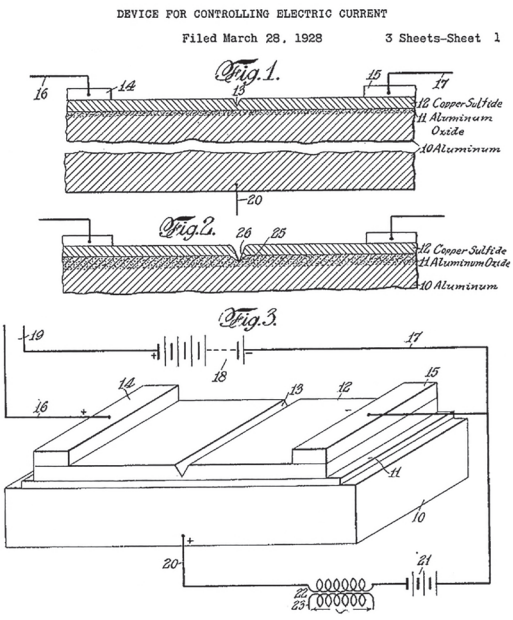


Fig. 4.3 Key component images (II) of the patent that laid the foundation for today's FET.
(Reprinted from U.S. Patent 1900018[3].)

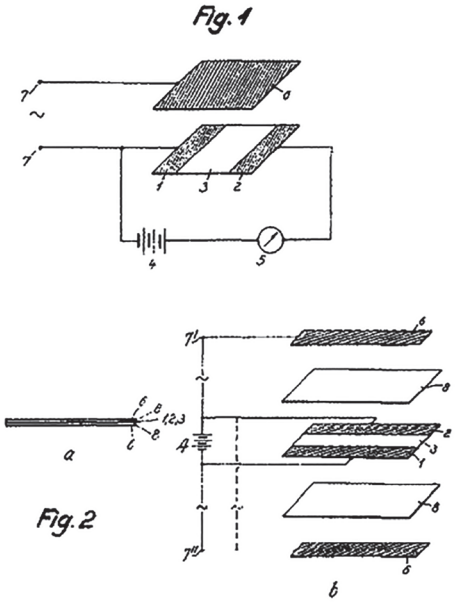


Fig. 4.4 Key component images of the patent that laid the foundation for today's MIS-FET.
(Reprinted from G. B. Patent 439457[5].)

The time would then come when the door would open widely to true semiconductor transistors. Mervin Joseph Kelly, the head of research at Bell Laboratories (official name at the time was "Bell Telephone Laboratories", hereinafter abbreviated as Bell Labs), recognized the limitations of vacuum tubes. He had high hopes for solid-state devices using semiconductors to replace vacuum tubes and hired William Shockley in 1936. After the war ended, solid-state physics theorist John Bardeen joined Shockley's team and began joint research with Walter Hauser Brattain and others in October 1945. Thanks to Kelly's precise management, on December 16, 1947, Bardeen and Brattain succeeded in amplification experiments[6] with the first point-contact transistor using high-purity germanium (Ge). A patent application was filed on July 17, 1948, and the patent was registered[7] on October 3, 1950. Fig. 4.5 shows representative drawings of that patent.

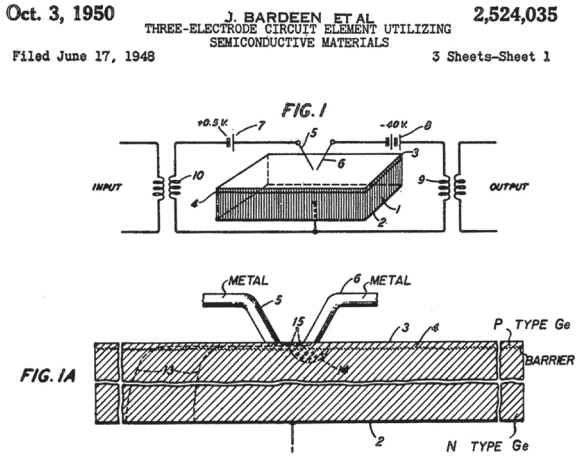


Fig. 4.5 Key component images of the patent regarding the invention of a point-contact transistor.
(Reprinted from U.S. Patent 2524035[7].)

The results of this research by Bardeen and Brattain arose from the process of examining the reason why a large modulation of current could not be obtained in the experiments[8] previously conducted by Shockley. On the other hand, Shockley invented the junction transistor the following year, in June 1948, filed a patent application on June 26, 1948, which was granted[9] on September 25, 1951, and the junction transistor became the basic model for bipolar transistors[10]. The representative component of that patent is shown in Fig. 4.6.

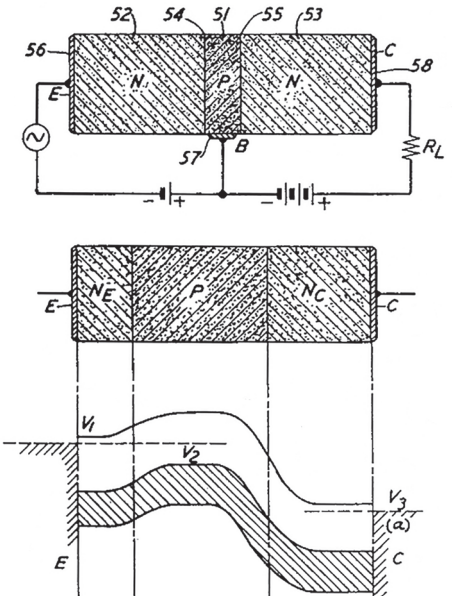


Fig. 4.6 Key component images of the patent that laid the foundation for today's bipolar transistor.
(Reprinted from U.S. Patent 2569347[9].)

In 1956, Bardeen, Brattain, and Shockley were awarded the Nobel Prize in Physics[11] for their invention of the transistor. A photograph of Bardeen, Brattain, and Shockley is shown in Fig. 4.7.

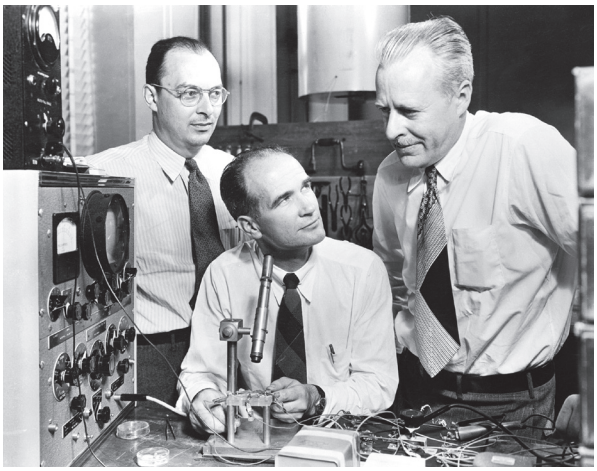


Fig. 4.7 Photograph of John Bardeen (left), William Shockley (center) and Walter Brattain (right) in Bell Laboratory.
(Source: Wikimedia Commons[11])

Column: Important Literatures and Internet Information from the Early Days of Semiconductor Engineering Development

The various information and related materials on the early days of semiconductors, which is the starting point of today's electronics, are briefly introduced in the following bullet points.

○ The detailed historical transition of semiconductor electronics from the dawn of the semiconductor industry to the present day is summarized in an organized form at the following URL, along with the work of its developers. (Viewed on 05.08.2022).
THE SILICON ENGINE −A TIMELINE OF SEMICONDUCTORS IN COMPUTERS−
https://www.computerhistory.org/siliconengine/

○ For more information on the history of semiconductors, including the early days of semiconductors, Kosuke Okuyama, former chief engineer of Renesas Technology Corporation, contributed the article "Story of Semiconductor", from the May 2008 issue until November 2014, a total of 34 articles to the SEAJ Journal, which published by Semiconductor Equipment Association of Japan (SEAJ). This article is in Japanese but should be referenced with the above information.
Story of Semiconductor
https://floadia.com/jp/column/ [in Japanese] (Viewed on 05.08.2022)

○ In addition, the history of Japan's semiconductor development is covered in a detailed article on the website of the Semiconductor History Museum of Japan.
Semiconductor History Museum of Japan
https://www.shmj.or.jp/ [in Japanese] (Viewed on 05.08.2022)
* In particular, the "Stories of Development Challenges" column on its website includes the above-mentioned article contributed by Dr. Okuyama.
Stories of Development Challenges: - Story of Semiconductor -
https://www.shmj.or.jp/dev_story/seaj.html [in Japanese] (Viewed on 05.08.2022)

○ Furthermore, each of the following literature sources provides information on research trends in semiconductor materials & device technology at that time.

- William F. Brinkman, Douglas E. Haggan and William W. Troutman:
"A history of the invention of the transistor and where it will lead us", IEEE J. Solid-State Circuits, 32, <12>, 1858-1865 (1997).
- Makoto Kikuchi: "History of semiconductor research – Course of events related to transistors and ICs -", OYO-BUTURI, 69, <8>, 913-918 (2000). [in Japanese]
- Makoto Kikuchi: "Memorable People in Semiconductor Research − Lessons Learned from Key Researchers −", Society of Semiconductor Industry Seniors News Letter, No.50 (April 2007). [in Japanese]
- Hajimu Kawamura: "Development of Semiconductor Physics in Half Century", OYO-BUTURI, 51, <2>, 112-116 (1982). [in Japanese]
- Yukio Shimura: "Commemorating the 15th Anniversary of the Founding of the Society of Semiconductor Industry Specialists; 65 Years of Semiconductor Development in Japan", Society of Semiconductor Industry Specialists "Encore", No.81, 5-9 (Oct. 2013). [in Japanese]
- Masakiyo Matsumura: "Thin-film transistors – From the past to the future –", OYO-BUTURI, 65, <8>, 841-848 (1996). [in Japanese]
- Michio Hatoyama: "Chapter 1 Materials for Electronics, Semiconducting Materials", Journal of the Japan Society for Testing Materials, 6, <41>, 60-69 (1957). [in Japanese]
- Yasuo Kanai: "Compound Semiconductors", J. Electrochem. Soc. Jpn., 28, 280-285 (1960). [in Japanese]
- Leo Esaki: "Birth and Development of Semiconductor Devices", Butsuri, 34, <3>, 203-213 (1979). [in Japanese]
- Renkazu Takiguchi: "Introduction to", Tokyo Denki University Press (Published May 20, 1979, 1st edition, 17th printing) [in Japanese]
- Hiroe Osafune: "Semiconductor History, (C&C Library)", Nippon Electric Culture Center Publishing Co., (1987). [in Japanese]
- Yoshitaka Furukawa: "History of Semiconductors", Journal of the Japan Institute of Metals, 29, <1>, 18-21 (1990). [in Japanese]

On the one hand, Heinrich Welker[12] of Siemens-Schuckert proposed that "semiconductors exist beside silicon". Welker, in his papers[13), 14)] of 1952 and 1953, explicitly states that AIP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb, etc., are candidates as semiconductors to replace Si and Ge. It is considered that these proposals led to vigorous research into group III-V compound semiconductor materials, leading to the development of today's semiconductor light-emitting diodes (LEDs) and semiconductor lasers (Laser Diode: LD).

After the invention of the transistor by the three researchers at Bell Labs, semiconductor devices shifted significantly toward silicon and the research on oxides and chalcogenide compounds such as CdO, CuS, CdSe, Cu_2O, and V_2O_5, which were used in early research, did not contribute significantly to the industry, and entered an era of basic (steady) research into semiconductor characteristics due to non-stoichiometry, oxygen defects, etc. Various research results and literature from that era have been compiled into many books and review papers[15), 16), 17)].

Later, in 1960, Dawon Kahng[18)] and Mohamed Martin Atalla18) of Bell Labs invented MOS-FET (Metal-Oxide-Semiconductor FET)[19), 20), 21)], which is the basic component device of the semiconductor devices today. Fig. 4.8 shows the photographs of both the researchers and Fig. 4.9 shows the image of typical components mentioned in the patent specification of MOS-FET. The subsequent papers[22), 23)] clearly describe the research and development of MOS-FET at that time.

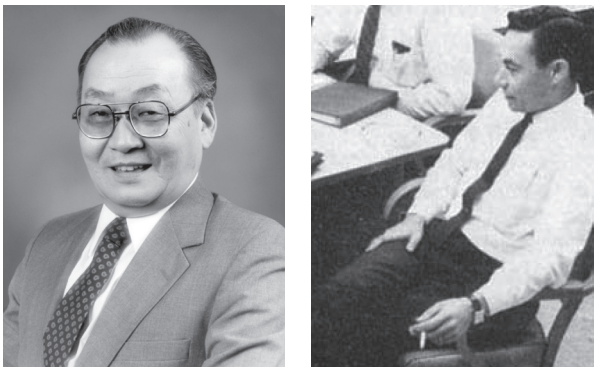


Fig. 4.8 Dawon Kahng (left) and Mohamed Martin Atalla (right)
(Source: Wikimedia Commons[18)])

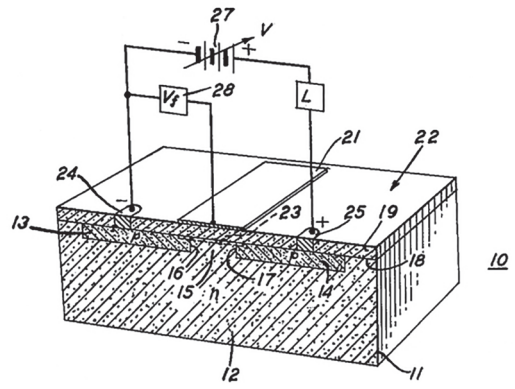


Fig. 4.9 Key component images of the patent that laid the foundation for today's MOS-FET.
(Reprinted from U.S. Patent 3102230[19)].)

In 1962, Paul K. Weimer[24)] of the RCA Laboratory announced the first thin-film transistor (TFT) using CdS as the semiconductor layer and calcium fluoride (CaF_2) as the gate insulator on a glass substrate. Fig. 4.10 shows the image of the components of the TFT depicted in the patent that Weimer filed in Japan at the time. Subsequently, the application of CdS-CdSe to imaging devices has been reported, and Weimer of RCA is considered to have marked the beginning of TFT technology[25), 26), 27)].

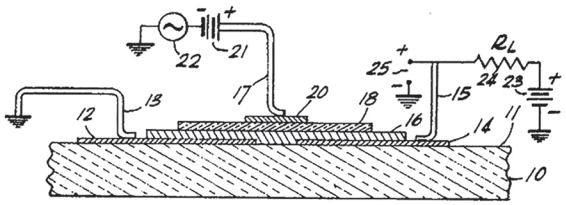


Fig. 4.10 Key component images of the patent that laid the foundation for today's thin film transistor (TFT).
(Reprinted from Japanese Registered Patent No. Sho 40-016459[27)].)

Even into the 1960s, CdS and CdSe were still used as semiconductors instead of Si. The situation at that time can also be seen in Okuyama's commentary[28)]. Under such circumstances, in 1964, Philips Research Institute[29)] reported a TFT using SnO2 as the channel layer. Further, in 1968, a team from Northwestern University reported on a TFT using ZnO single crystals and reported a Hall mobility of 220 cm^2/Vs[30)]. It is assumed that SnO_2 or ZnO used as the semiconductor channel in these reports did not present the technological seeds that would lead to significant development of subsequent research because the technology at that time for fine material control of interfaces, grain boundaries, and oxygen defects was not as advanced as it is today.

In 1971, the concept of Active-Matrix Liquid Crystal Display (AM-LCD) was proposed by Bernard J. Lechner[31)] et al. of the RCA Laboratory[32)]. (See Fig. 4.11)

Then, to realize the AM-LCD proposed by Lechner, a 6-inch square 14,000-pixel liquid crystal display using TFTs with CdTe, a cadmium compound, as the channel layer, which was still a familiar research subject initially, was developed[34)] by T. Peter Brody[33)] et al. of Westinghouse. (See Fig. 4.12)

Fig. 4.11 Bernard J. Lechner.
(Source: Wikipedia[31)])

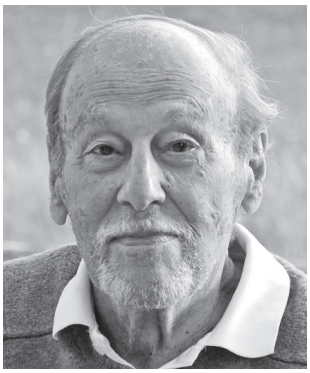


Fig. 4.12 T. Peter Brody
(Source: Wikipedia[33])

Such major developments in AM-LCD technology in displays also coincided, and there was a prolonged gap concerning notable research publications on oxide TFTs.

In 1975, Walter Eric Spear[35] of the University of Dundee, Scotland, succeeded in fabricating the world's first thin film of amorphous silicon by decomposing silane (SiH_4) using the so-called plasma CVD method that uses glow discharge[36), 37)]. At this stage, Spear also doped phosphorus (P) and boron (B) to form a semiconductor thin film, which was an extremely important research result. Finally, in 1979, (Peter George Le Comber)[38] reported[39] that a-Si TFT could be fabricated on a glass substrate using the plasma CVD method developed by Spear et al. His report is the origin of the a-Si TFT technology currently used for flat-panel displays.

Since then, research and development on amorphous silicon thin film transistors has been firmly established in display applications, and intensive research is being conducted from various angles. The reports by Kazuo Morigaki[40), 41), 42)] and the commentary by Eiichi Maruyama[43] are interesting materials in that they provide an overview of the research situation at the time.

Later, in 1986, Sameshima et al. of Sony Central Research Laboratories were able to fabricate a polysilicon (polycrystalline silicon) TFT using excimer laser annealing with a wavelength of 308 nm under a low-temperature process of 260°C, achieving a high mobility of 180 cm^2/Vs[44]. The research results created a technological trend that significantly surpassed the mobility of a-Si TFTs and was the starting point of TFTs that use crystalline silicon as the channel. Clearly demonstrating the high characteristic values of crystalline silicon TFTs had great significance, and the research results can be said to be the starting point for the laser annealing technology, which became a technological trend thereafter. In addition, this was certainly a great motivation for the research and development of LTPS (Low Temperature Poly Silicon)-TFT, which has become well-known today. However, when trying to obtain large-area crystalline silicon thin films with high characteristics, the large-area laser beam for annealing and the uniformity of its intensity become major obstacles, due to which, the TFTs, despite their high characteristics, are not very suitable for large-area applications.

A few years later, in 1989, Gary Stix of IBM Japan made an announcement[45] regarding large-area LCD panels, a technological trend that attracted considerable industry attention. In effect, the LCD panel business using a-Si TFTs made significant progress internationally.

Liquid crystal display and thin film transistor technologies are the two wheels of a cart, and many papers and commentaries describe them in detail[46), 47), 48)].

In 1991, just as the "high-temperature superconducting fever" had finally subsided and the research on essential physical properties was moved forward, a paper on MIS-FET-type field-effect transistors with the channel layer of $YBa_2Cu_3O_{7-\delta}$, which was well known as a high-temperature superconducting material to those involved, and a gate insulating layer of $SrTiO_3$ with the same perovskite crystal structure was submitted by a group of four researchers at the IBM Zurich Research Laboratory in Switzerland, which reported that carrier modulation was possible[49]. Two of these four researchers, J. G. Bednorz and K. A. Müller, were awarded the Nobel Prize in Physics in 1987 for discovering high-temperature superconducting materials[50]. Later, in 1995, Yukio Watanabe of Mitsubishi Kasei Corporation reported[51] on a ferroelectric transistor with an all-perovskite stacked structure in which $(LaSr)_2CuO_4$, a typical Hall-conductive high-temperature superconducting oxide was used as the channel layer, and a ferroelectric PLZT [=$(PbLa)(ZrTi)O_3$] thin film epitaxially grown on top of that, as the gate insulating layer. This was around the time when the concept of oxide electronics was also about to take off, and proved to be a classic example was the construction of a device in which the entire system from the channel layer to the insulator (ferroelectric) was epitaxialized by utilizing epitaxial single crystal growth technology[52] refined in the field of oxide electronics. Subsequently, research on electric field modulation using three-terminal devices using high-temperature superconducting oxide as a channel was positioned as an important basic research field for the field effect with respect to strongly correlated materials amid the major technological trend of oxide electronics. For example, a three-terminal device using a high-temperature superconducting material as the active layer, which was jointly researched by Ahn of Yale University, Triscone of the University of Geneva, and Mannhart of the University of Augsburg, is a typical reported example[53].

At a time when amorphous silicon thin film transistors were at their peak, and many researchers of solid-state physics and materials science were riding the technological trend of oxide electronics aiming to investigate the physical properties of single-crystal thin films grown epitaxially in the field of functional oxides, Hideo Hosono of the Tokyo Institute of Technology proposed an important Working Hypothesis[54] for materials design to explore wide-gap oxide semiconductors, at the 16th International Conference on Amorphous Semiconductors (ICAS-16) held in Kobe in September 1995. As explained in Chapter 3, this hypothesis shows that amorphous composite oxides composed of heavy metal cations with an electronic configuration of $(n-1)d^{10}ns^0$ are promising candi-

dates for new amorphous semiconductor materials. A group of materials, including a-$AgSbO_3$, Cd_2GeO_4, and Cd_2PbO_4, were verified electrically and optically to prove this hypothesis. However, contrary to Hosono's feelings, this presentation generated very little interest[55]. Almost all activities at Hosono's Laboratory at the Tokyo Institute of Technology from the mid-1990s to the early 2000s had started with this Working Hypothesis presented at ICAS-16, and in addition to the verification of the hypothesis, research was expanded toward further development and innovation as described in detail in the previous chapter.

Meanwhile, similar research using a ferroelectric material for the gate insulator was reported by Phillip's group[56]. This is the first presentation of a transistor using the SnO_2 channel layer in 32 years. This study pertains to an all-oxide ferroelectric TFT with an Sb-doped SnO_2 layer as the semiconductor channel, a ferroelectric PZT [= $Pb(ZrTi)O_3$] thin film as the gate insulator, and a conductive perovskite $SrRuO_3$ film as the gate electrode.

Since then, thanks to the growing opportunity and technological improvements in oxide electronics, several research institutes worldwide have reported research on ZnO-based thin film transistors. One of the major features of oxides is that they can be fabricated into thin films through a solution process. This film deposition method does not use the vacuum chamber used in the pulsed laser deposition and sputtering methods reported so far. In 2001, Yutaka Ohya et al. of Gifu University deposited a thin ZnO film (40 nm) on a Si wafer (with a thermal oxide film) using a chemical solution deposition process using zinc acetate ($Zn(OCOCH_3)_2 \cdot 2H_2O$) as raw material to fabricate a bottom-gate ZnO-TFT via the solution-process[57]. This report on oxide semiconductor transistors via the solution-process is considered the first in this technology area. This method, which does not use a vacuum chamber, is quite appealing to researchers worldwide. Since Hosono's publication in *Nature* in 2004, there has been significant technological development from around 2010. In particular, considerable research has been reported on the In-Ga-Zn-O system alone[58)-72)]. Furthermore, many papers[73)-90)] have been published on solution-processed TFTs targeting other related material systems, and there is even a comprehensive report[91)] on the fabrication of heterojunctions using this solution-process method. Given the actual progress in this field, the paper by Ohya et al.[57)] published in 2001 is considered an important paper that served as the starting point for solution-processed oxide thin film transistors.

Returning to the vacuum process, ZnO-TFT was presented in 2003 by the research group of Tomoji Kawai at the Institute of Scientific and Industrial Research, Osaka University[92)]. According to the reported data, this is a bottom-gate type thin-film transistor using a [SiO_2/SiNx] bilayer gate insulator with a relatively high on-off ratio of 5 orders of magnitude. In addition, a research group in the United States, which, like Hosono was interested in transparent oxide semiconductor devices, also reported regarding TFT using a ZnO layer as a channel[93)]. The joint research on ZnO-TFT by R. L. Hoffman of Hewlett-Packard Company and J. F. Wager of Oregon State University reported that the mobility was approximately 2.5 cm^2/Vs. Furthermore, a research group led by Masashi Kawasaki, who was working at the Institute for Materials Research, Tohoku University, at the time, fabricated a TFT by placing a CaHfOx layer between the SiN gate insulator and the ZnO channel layer and reported a mobility of 7 cm^2/Vs at a process temperature below 300°C[94)]. It should be noted that the research group of Kawasaki subsequently improved the field-effect mobility to about 70 cm^2/Vs by using a ZnO single-crystal thin film with improved lattice matching using a $ScAlMgO_4$ substrate[95)]. Furthermore, around the same time, the research group of E. Fortunato in Portugal presented a ZnO-TFT with field-effect mobility of 70 cm^2/Vs at [The 20th International Conference on Amorphous and Microcrystalline Semiconductors (ICAMS 20)] held in August 2003, which was published in a paper in 2004[96)]. It is indeed curious that in 2003, after a gap of 35 years since the announcement of ZnO-TFT by the Northwestern University group in 1968, several research institutions worldwide continued to report on TFT using the same ZnO. The 35-year hiatus is undoubtedly due to the difficulty in controlling ZnO-specific oxygen defects and interstitial Zn ions, the existence of ZnO-specific potential barriers at grain boundaries and interfaces, and the fact that no specific method has been found to resolve these issues. However, it is believed that the question of what kind of technology was being used to overcome the various challenges unique to ZnO after 2003, is yet to be dispelled.

Meanwhile, in the same year, Hosono's group, which was leading the ERATO project, had discovered various materials and accumulated technology and confirmed that the p-type semiconductor $ZnO \cdot Rh_2O_3$ could function even in an amorphous state, which led them to obtain excellent diode characteristics[97)], successfully with data showing an on-off ratio of 3 orders of magnitude by implementing a p-n junction with amorphous $InGaZnO_4$, an n-type oxide semiconductor. The success of the p-n junction while maintaining the amorphous state of both p-n phases is extremely significant, and it also served as a major turning point in the ascent to functional devices equivalent to amorphous silicon. This achievement of the world's first all-amorphous oxide p-n junction[97)] served as the basis for the subsequent presentations of transistors. The research results form the basis for amorphous oxide electronic device technology, which is extremely important to many materials researchers.

In May 2003, a transparent oxide semiconductor transistor using homologous crystalline phase $InGaO_3(ZnO)_m$ (m = integer) as the channel was published in *Science*[98)]. The Reactive Solid-Phase Epitaxy Method[100)-104)] invented[99)] by Hiromichi Ohta, a co-researcher in ERATO "HOSONO Transparent ElectroActive Materials Project", was behind this technological achievement, and an extremely effective technology for epitaxially grown single-crystalline channel layer. The mobility value of TFT using this $InGaO_3(ZnO)_5$ epitaxial

Historical flow of transistors focusing on semiconducting materials up to the discovery and invention of a-IGZO TFT

◆ **FET**
Julius Edgar Lilienfeld
Semiconductor: Cu_2S (CuS)
U. S. Patent 1745175 (1926-1930)
U. S. Patent 1900018 (1928-1933)

◆ **MIS-FET**
Oskar Heil
Semiconductor: Te, I_2, Cu_2O, V_2O_5
G. B. Patent 439457 (1935-1935)

◆ **Point-Contact Transistor**
John Bardeen (Bell Lab.)
Walter Hauser Brattain (Bell Lab.)
Semiconductor: Ge
U. S. Patent 2524035 (1948-1950)

◆ **Junction-type Transistor**
William Shockley (Bell Lab.)
Semiconductor: Ge
U. S. Patent 2569347 (1948-1951)

◆ **III-V Compound Semiconductors Proposal**
Heinrich Welker (Siemens-Schuckert)
Candidates: AIP, AlAs, AlSb, GaP, GaAs, GaSb, InP, InAs, InSb
Z. Naturforschg., 7a, 744-749 (1952).
Z. Naturforschg., 8a, 248-251 (1953).

◆ **MOS-FET**
Dawon Kahng (Bell Lab.)
Semiconductor: Si
U. S. Patent 3102230 (1960-1963)
Mohamed M. Atalla (Bell Lab.)
Bell Sys. Tech. J., 38, 749-783 (1959).
IRE-AIEE Solid-State Device Res. Conf., (1960).

◆ **Thin Film Transistor (TFT)**
Paul K. Weimer (RCA)
Semiconductor: CdS-CdSe
Proc. IRE., 50, <6>, 1462-1469 (1962).
Proc. IEEE, 55, <9>, 1591-1602 (1967).
Japanese Patent (Toku Kou Shou) 40-016459 (1962-1965) [in Japanese]

◆ **SnO_2-TFT**
H. A. Klasens and H. Koelmans (Philips)
Solid State Electronics, 7, <9>, 701-702 (1964).

◆ **ZnO-TFT**
G. F. Boesen and **J. E. Jacobs** (Northwestern U.)
Proc. IEEE, 56, <11>, 2094-295 (1968).

◆ **AM-LCD Proposal**
B. J. Lechner, et. al., (RCA)
Proc. IEEE., 59, 1566-1579 (1971).

◆ **CdTe-TFT 20 lines/inch**
T. P. Brody et al., (Westinghouse)
IEEE Trans. Elec. Dev., ED-20, 995-1001 (1973).

◆ **a-Si Thin Films by Plasma CVD**
W. E. Spear et al., (Univ. Dundee)
Solid State Commun.,17, <9>, 1193 (1975).
Appl. Phys. Lett., 28, <2>, 105 (1976).

◆ **a-Si TFT for LCD**
P. G. Le Comber et al., (Univ. Dundee)
Elec. Lett., 15, <6>, 179-181 (1979).

◆ **Poly-Si TFT by Excimer Laser Annealing**
T. Sameshima et. al., (SONY)
IEEE Elec. Dev. Lett., 7, 276-278 (1986).

◆ **$YBa_2Cu_3O_{7-d}$-TFT with $SrTiO_3$ Gate**
J. Mannhart, J. G. Bednorz, K. A. Müller
and **D. G. Schlom** (IBM Zurich Res. Lab.)
Z. Physik B, 83, 307–311 (1991).

◆ **$(LaSr)_2CuO_4$-TFT with PLZT-Ferroelectric Gate**
Yukio Watanabe, (Mitsubishi Chemical)
Appl. Phys. Lett., 66, 1770-1772 (1995).

↳ ◆ **$GdBa_2Cu_3O_{7-\delta}$-TFT with $(BaSr)TiO_3$ Gate**
C. H. Ahn, J.-M. Triscone and J. Mannhart
Nature, 424, 1015-1018 (2003).

◆ **Proposal on Novel Transparent Amorphous Oxide Semiconductors**
Hideo Hosono
16th-ICAS at Kobe, (1995.09.04-08)
J. Non-Cryst. Sol., 198–200, 165-169 (1996).
※ Amorphous oxides composed of heavy metal cations with an electronic configuration of **$(n-1)d^{10}ns^0$**

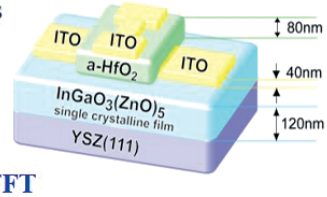
◆ **SnO_2:Sb-TFT with PZT-Ferroelectric Gate**
M. W. J. Prins, et al., (Philips)
Appl. Phys. Lett., 68, 3650-3652 (1996).

◆ **ZnO-TFT (Solution-Process)**
Yutaka Ohya's Gp.:
Jpn. J. Appl. Phys., 40, 297-298 (2001).

◆ **ZnO-TFT**
Tomoji Kawai's Gp.: J. Appl. Phys., 93, 1624 (2003).
John F. Wager's Gp. (Oregon State Univ.):
Appl. Phys. Lett., 82, <5>, 733-735 (2003).
Masashi Kawasaki's Gp.:
Jpn. J. Appl. Phys., 42, <4A>, L347-L349 (2003).
Adv. Mater., 16, <21>, 1887-1890 (2004).
Elvira Fortunato's Gp. (New Univ.Lisbon):
20th-ICAMS at Campos do Jordao (2003).
J. Non-Cryst. Sol., 338-340, 806-809 (2004).

◆ **All Amorphous p-$ZnO{\cdot}Rh_2O_3$/ n-IGZO Heterojunction Diode**
Hideo Hosono's Gp. [JST-ERATO]
Adv. Mater., 15, <17>, 1409-1413 (2003).

★ **Crystal Homologous $InGaO_3(ZnO)_m$-TFT**
Hideo Hosono's Gp. [JST-ERATO]
"Thin-Film Transistor Fabricated in Single-Crystalline Transparent Oxide Semiconductor",
Science, 300, 1269–1272 (2003).
※ Mobility μ ~ 80 cm^2/Vs



★ **Amorphous $InGaZnO_4$-TFT**
Hideo Hosono's Gp. [JST-ERATO-SORST]
"Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors",
Nature, 432, 488-492 (2004).
※ Mobility μ = 6 ~ 9 cm^2/Vs

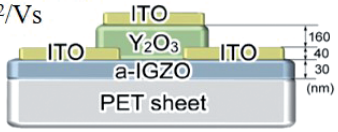


Fig. 4.13 Historical flow of transistors focusing on semiconducting materials up to the discovery and invention of a-IGZO TFT.
(The drawings of the two transistors in this historical flow are courtesy of Prof. Hideo Hosono.)

single-crystalline phase was 80 cm^2/Vs. The on-off ratio was about 6 orders of magnitude, which was close to that of single-crystal silicon (~100 cm^2/Vs), a significant achievement for a thin film transistor using oxide crystal as a channel layer and a major epoch-making event in materials science. This achievement is equivalent to demonstrating one of the highest attainable points in functional oxides. The publication by Hosono's group in *Science* attracted worldwide attention with Wager from Oregon State University, who, like Hosono, had published ZnO-based TFTs aimed at transparent electronics, publishing an urgent commentary[105] titled "Transparent Electronics" in the same magazine, showing that the publication by Hosono et al., of the ERATO research project group was extremely noteworthy.

They confirmed the operation of a transistor with a very simple composition ratio of In:Ga:Zn = 1:1:1, unlike a series of homologous materials, and mobility of 6 to 9 cm^2/Vs by using an amorphous thin film instead of a crystal for the channel layer, and the research results were published[106] in *Nature* in November 2004. This was the first amorphous oxide TFT in the world. Compared to amorphous silicon, the electron mobility is at least ten times higher, and the degree of property deterioration due to amorphization was suppressed more than expected, resulting in satisfactory property values. Therefore, this led to significant expectations for flexible electronics products due to (1) expectations for new transparent electronics products such as transparent displays, (2) the possibility of low-temperature processing (can be supported with processes similar to that of the current amorphous silicon), and (3) ability to be applied on organic material substrates that can be bent. There is no doubt that the presentation of the amorphous IGZO-TFT in *Nature* paper received more worldwide attention than the one in *Science* paper, which deals with crystals, not only at conferences but also among people involved in the global electronics industry. The research results had an extremely significant impact on electronics and other industries worldwide.

A brief description of the history of semiconductor transistors from their origin is given above. Fig. 4.13 summarizes the historical flow of semiconductor transistors in a single drawing.

The author was reminded once again of the impression he has of Hosono Hideo, a pioneer of IGZO-based oxide semiconductor materials, as a unique researcher who, even in the face of criticism, tenaciously stuck to his own beliefs and pushed forward with his research, and at times drew on his unique sensibilities to open up the door to new scientific principles. In addition, at least for the period of about 12 years from around 1992 to 2004, particularly during the research period of the ERATO "HOSONO Transparent ElectroActive Materials Project", part of the JST Strategic Basic Research Program, there is no doubt that Hosono, as the research director, demonstrated great skill in organizing the project and communicating with the members to nurture them. I sincerely hope that Hosono will continue to make significant advances in research in the future, not only for himself but also for the members who have graduated under his tutelage.

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   - Walter H. Brattain: (Viewed on 08.01.2022). https://www.nobelprize.org/uploads/2018/06/brattain-lecture.pdf
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• Photograph (right) source of Mohamed Martin Atalla https://commons.wikimedia.org/wiki/File:Atalla1963.png (Viewed on 10.14.2022)
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5 Significance of Creation on IGZO-Based Transparent Oxide Semiconductor Thin-Film Transistor

5.1 Significance of Publication in *Science* Paper

The announcement in *Science* paper, published on May 23, 2003, presented the world with a thin-film transistor using a very high-performance transparent oxide semiconductor: $InGaO_3(ZnO)_5$ for the channel layer, which clearly demonstrated one achievement in oxide semiconductors, that is, instead of the conventional amorphous silicon transistors, if a clean epitaxial oxide single crystal thin film is created as a channel layer and the carrier concentration is appropriately controlled, a higher performance transistor characteristics can be obtained. This paper is of great significance in materials science and will have an enormous ripple effect on materials technology as well[1].

The "reactive solid-phase epitaxial growth method" developed independently with the ERATO "HOSONO Transparent ElectroActive Materials Project" under the Creation Science Promotion Project of the Japan Science and Technology Corporation (JST, currently the Japan Science and Technology Agency) was applied to the single-crystallization of $InGaO_3(ZnO)_5$ thin films, which are homologous transparent oxide semiconductors, and single-crystal $InGaO_3(ZnO)_5$ thin films were epitaxially grown on single-crystal Yttria-Stabilized Zirconia (YSZ) substrate. By utilizing the epitaxially grown single-crystal thin film as the electron channel layer for semiconductors and selecting a high-dielectric-constant material like HfO_2 for the gate insulator, the researchers realized a high-performance transparent field-effect transistor (TFET) with excellent normally-off characteristics (meaning there is no current flow between source and drain when no electric field is applied to the gate) and an extremely high electron mobility of approximately 80 cm^2/Vs in the channel[1), 2)].

The reason why we chose the $InGaO_3(ZnO)_m$ system instead of the $In_2O_3(ZnO)_m$ system as the electron channel layer is thought that the Hosono group wanted to avoid the In-rich side with excessively high electrical conductivity or to suppress the carrier concentration a little more from the viewpoint of the function as a semiconductor film, not as a transparent conductive film. Furthermore, the author imagines that the reason for the choice of the In:Ga=1:1 composition may have been due to the many important crystal structure chemistry results[3), 4), 5), 6), 7)] accumulated by Noboru Kimizuka et al. in the past, in which the In:Ga=1:1 composition is thought to be thermodynamically stable. The choice of this In:Ga=1:1 composition was also directly related to the normally-off function required for the transistor. The paper in *Science* also clearly states that the incorporation of Ga will not cause Zn-site substitution and the generation of electron carriers. The correctness of this concept is evident in the results of a study of the correlation between the [In]/([In]+[Ga]) ratio and electrical conductivity in $In_{1-x}Ga_{1+x}O_3(ZnO)_m$, published as a joint work by Moriga and Poeppelmeier[8)] after Kimizuka's report on crystal structure chemistry.

This groundbreaking work, originating from JST's unique ERATO project and led by Hosono, which was featured in a *Science* paper, showcased the remarkable "potential" of $InGaO_3(ZnO)_m$-based oxides. It illuminated the promising future of these materials, which had previously remained unexplored and opened up new avenues for subsequent exploration. While a lower gallium (Ga) concentration is preferable regarding conductivity, the researchers intentionally opted to suppress conductivity to facilitate the creation of transistors. Previous attempts to create transistors using SnO_2 and ZnO have been announced several times; producing high-quality, stable transistors that exhibit normally-off characteristics was difficult because oxygen defects are easily generated in the materials. However, the high-quality crystalline $InGaO_3(ZnO)_5$ transistor developed this time has an on/off ratio of 6 orders of magnitude, demonstrating very good transistor characteristics.

One of the key technologies that enabled this success was the reactive solid-phase epitaxy method devised[9)] by Hiromichi Ohta from Hosono's group[10), 11), 12), 13)]. Ohta was awarded the Progress Award by the Ceramic Society of Japan in 2005 for his pioneering work on this technique[14)]. The high-quality single-crystal thin films obtained through this technique effectively suppressed excessive oxygen defects, leading to enhanced device stability and solidifying the research results. A cross-sectional transmission electron microscopy image of the high crystalline quality of the epitaxially grown thin film is shown in Fig. 5.1.

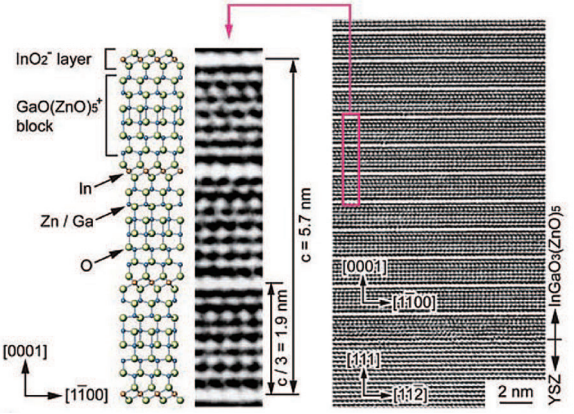

Fig. 5.1 Cross-sectional structure of epitaxially-grown single crystalline $InGaO_3(ZnO)_5$ thin film on the YSZ (Y-stabilized zirconia) single crystal substrate. Illustration (left) to easily understand how they are stacked in layers and crystal lattice image (right) by high-resolution transmission electron microscopy (HR-TEM). (These illustration and TEM photographs are courtesy of Prof. Hideo Hosono.)

In this case, to fabricate the $InGaO_3(ZnO)_5$ epitaxial thin film on a single-crystal YSZ substrate, the transistor structure had to be a top-gate configuration, which imposed certain constraints. Furthermore, to maximize the functional potential of these homologous oxide semiconductor crystals, the entire thin film on the substrate must undergo a high-temperature annealing at 1400°C during the initial stages of the device fabrication process. In other words, this technique is not suited to be discussed for industrial-scale applications. Given this background, the research results should be discussed from the standpoint of pure materials science rather than debating its potential for industrial applications.

Fig. 5.2 (a) and (b) illustrate the structure and appearance of the fabricated transistor.

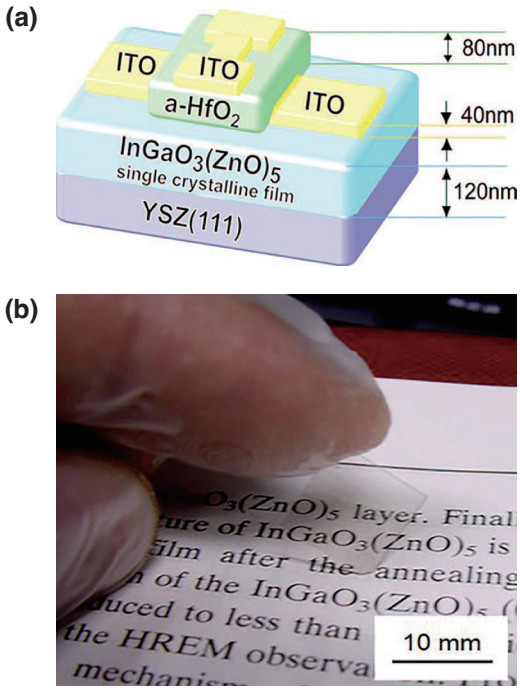

Fig. 5.2 Image (a) of the transistor using epitaxial single crystalline $InGaO_3(ZnO)_5$ thin film on a YSZ single crystal substrate and the photograph (b) of this transparent thin film transistors.
(These illustration and photographs are courtesy of Prof. Hideo Hosono.)

The choice of hafnium oxide (HfO_2) as the gate insulator, an important component of transistors, was appropriate since HfO_2 has gained significant attention in recent years due to its high dielectric constant of approximately 20. Using the same oxide for the channel layer and the gate insulator likely contributed to minimizing defects at the interface between these two components. While oxide materials are commonly used as gate insulators in conventional silicon semiconductors, using the same oxide material as the channel layer for the gate insulators could intrinsically provide a significant advantage in reducing interface defects. As a result, the transistor achieved an electron mobility as high as 80 cm^2/Vs, which is more than 2 orders of magnitude higher than amorphous silicon and close to the performance of polycrystalline silicon TFTs. Furthermore, ITO films are used as transparent electrodes for all three electrodes (source, drain, and gate). To begin with, since the Hosono Group has accumulated epitaxial growth technology for ITO films[15), 16)], the entire process is considered to have been completed as a total transistor device using the group's accumulated technologies.

The ITO epitaxial thin film technology developed by Ohta et al. of the Hosono group produces ITO thin films with an ultra-flat surface characterized by steps and terraces only 0.3 nm high. Furthermore, Sn dissolved perfectly in In_2O_3 and formed the solid solution; the defects at the crystal grain boundaries were minimal, with exceptional conductivity, reaching approximately 13,000 S/cm, among the highest in the world at the time[15)]. Moreover, the junction interface between ITO and $InGaO_3(ZnO)_m$ is presumed to be a highly compatible combination, as they share an indium layer having the same oxide structure. The Hosono group likely considered this point carefully before choosing the ITO electrode, resulting in a fully transparent oxide crystal semiconductor transistor composed entirely of transparent materials. The author's impression is that the meticulous accumulation of expertise within the Hosono group over many years paid off and materialized in the form of the groundbreaking publication in *Science* paper in 2003. Reflecting on this research journey, it is highly significant.

At this point, I want to give a perspective beyond the technical aspects. As mentioned in Chapter 3, the decision to recruit Hiromichi Ohta and Masahiro Orita as ERATO researchers played a crucial role. Hiromichi Ohta was a young researcher who first encountered the homologous system from the perspective of thermoelectric conversion materials while working in Professor Kunihito Koumoto's laboratory at Nagoya University[17)]. Subsequently, Ohta joined HOYA Corporation and collaborated with Noboru Kimizuka of the National Institute for Research in Inorganic Materials, co-authoring 2 papers (both with Orita as a co-author)[18), 19)]. It is considered that Ohta had already established himself as an expert in homologous oxides when he joined ERATO. On the other hand, Masahiro Orita, a researcher at HOYA, had early published papers proposing $InGaZnO_4$ crystal (not amorphous) as a potential next-generation transparent conductive material based on its electrical and optical properties[20), 21)]. Additionally, Orita co-authored another paper with Noboru Kimizuka, apart from the 2 co-authored with Ohta mentioned above[22)]. However, based on the available co-authored publications, it appears that HOYA's Ohta and Orita's collaboration with Kimizuka involved a different material system unrelated to transparent conductive materials. This arrangement may have been intended to avoid conflict with HOYA's research strategy on transparent conductive materials while allowing these two young researchers to become familiar with homologous oxides as promising candidates for such applications. Another noteworthy point is that Orita is likely to have significantly contributed to the development (or improvement) of

the pulsed laser deposition (PLD) equipment used extensively for the deposition of thin films in the early stages of the Hosono group's work[23].

Undoubtedly, Hosono's decision to involve these 2 researchers, who already had some knowledge about homologous oxides and their electrical properties, significantly contributed to the success of the ERATO project. In the spring of 2002, Orita returned to his original position at HOYA. However, this transition was seamlessly managed, with Kenji Nomura, a doctoral student at the Hosono laboratory since the previous year, taking Orita's place in the ERATO project. Nomura mastered the research accumulated within Hosono's group in a very short period of time and wrote a paper to be submitted to *Science* at an astonishing speed. The achievements of the Hosono project were truly a collective effort, with all members diligently passing on their expertise and working in unity over several years.

Hosono group had experienced the proposal of guidelines for material exploration of transparent p-type oxide semiconductors in 1997 and the fact that transparent p-type oxide semiconductors were actually discovered[24]. In the ERATO "HOSONO Transparent ElectroActive Materials Project" of JST, as mentioned above, a p-n junction was fabricated using transparent oxide semiconductor crystals, and the world's first ultraviolet light-emitting diode was demonstrated[25, 26].

The high-performance transparent oxide semiconductor thin-film transistor based on the single-crystal $InGaO_3(ZnO)_5$ material represents a significant milestone among the numerous important research accomplishments involving functional oxide crystal materials achieved by this project. Fig. 5.3 illustrates the detailed crystal structure of the single-crystal $InGaO_3(ZnO)_5$.

The achievement of creating a field-effect oxide transistor with an on/off ratio of around 6 orders of magnitude, with a normally-off characteristic, and electron mobility as high as 80 cm^2/Vs, comparable to that of polysilicon TFTs, by utilizing epitaxial oxide single crystal as the channel layer of transistors, can be considered state-of-the-art from a materials science perspective in the field of oxide electronics, which is a rapidly evolving trend of our time.

Today, this *Science* paper has garnered significant attention from materials researchers worldwide, with 1,713 citations according to Scopus and 2,895 citations on Google Scholar (as of October 5, 2022). As will be discussed in Chapter 7 of this report, the number of research initiatives inspired by this groundbreaking work from the Hosono group has increased dramatically.

However, it is important to note that the fabrication process for this oxide crystal transistor involved an annealing step at temperatures well above 1000°C, making it unsuitable for industrial-scale production. Consequently, a clear path toward industrialization was not yet evident. It can be easily presumed that Hosono was fully aware of these challenges. Hosono stated, "I didn't get into science to make people's lives better; my goal is to do work that is essential for life" during an interview with a reporter[27]. This unwavering passion and dedication paved the way for the groundbreaking work published in *Nature* magazine the following year, in 2004. Inspired by the remarkable electron mobility of approximately 80 cm^2/Vs achieved in the crystalline $InGaO_3(ZnO)_m$-based transistors presented in the *Science* paper, the thought "What kind of mobility could we achieve with amorphous materials?" may have gradually come to Hosono's mind as a simple curiosity. Regardless, the research achievements presented in the *Science* paper undoubtedly paved the way and served as a "grand prelude" to the groundbreaking work published in *Nature* paper a year later.

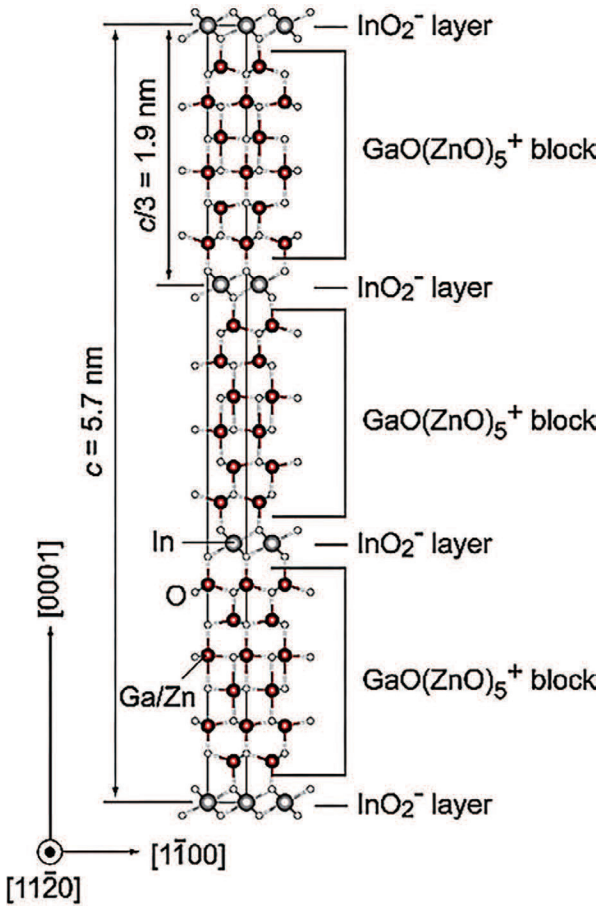

Fig. 5.3 Crystal structure of single crystal $InGaO_3(ZnO)_5$
(These illustration and photographs are courtesy of Prof. Hideo Hosono.)

5.2 Significance of Publication in *Nature* Paper

In September 1995, at the 16th International Conference on Amorphous Semiconductors (16th-ICAS (1995)) held in Kobe, Hosono set himself the challenging task of validating his working hypothesis[28]. The culmination of this endeavor materialized in the groundbreaking publication in *Nature* paper on November 25, 2004[29]. Hosono's research group triumphantly unveiled to the world a novel generation of oxide semiconductors based on amorphous oxide semiconductors with a wide energy gap and a moderate degree of conductivi-

ty, showcasing their potential to replace amorphous silicon in the form of a practical device, namely the field-effect transistor using an amorphous oxide semiconductor [29), 30)].

A brief discussion of the technical background leading to the discovery and invention of this amorphous IGZO-based oxide semiconductor suggests that one of the starting points can be traced back to the 1997 publication by Kawazoe and Hosono in *Nature* paper, where they introduced the p-type $CuAlO_2$ as the substrate for the fundamental pn junction in semiconductor devices[24)]. The success of the exploration guidelines into p-type oxides paved the way for the subsequent discovery of a chain of new p-type oxide semiconductors, including $SrCu_2O_2$, $CuGaO_2$, and $ZnRh_2O_4$.

Another crucial starting point was Hosono's "Working hypothesis", presented at the 16th International Conference on Amorphous Semiconductors (16th-ICAS), which emphasized the importance of the $(n-1)d^{10}ns^0$ electronic configuration of heavy metal ions. Under "Hosono's Working Hypothesis", various amorphous oxide semiconductors like a-$AgSbO_3$[31)], a-Cd_2GeO_4[32)], and a-Cd_2PbO_4[33)] were discovered sequentially. Furthermore, the amorphous phase of p-type conductive a-$ZnRh_2O_4$ was discovered, leading to the successful creation of an all-amorphous oxide pn junction. This information was published in Advanced Materials in 2003, a year before the publication in *Nature* paper[34)]. In this context, a-$InGaZnO_4$ emerged as the n-type amorphous oxide semiconductor counterpart to the p-type. The excellent conductive properties of the amorphous $InGaZnO_4$ oxide semiconductor had already been reported by Masahiro Orita, who had recently joined the ERATO project from HOYA, at the MRS International Conference[35)] in San Francisco in April 2000 and related publications[36)]. Therefore, it is easy to imagine that the success of pn junctions using only amorphous oxides was well grounded.

In a paper by Toshio Kamiya et al.[37)], which received the Special Prize at the 19th (2005) "Advanced Technology Award," the details of how they chose a-$InGaZnO_4$ are described. In Hosono's laboratory at that time, it is noted that they searched for materials in the In_2O_3-ZnO-Ga_2O_3 ternary oxides system that would enable control of the appropriate carrier concentration and mobility from the perspective of a semiconductor, which is very different from the position of conductive pursuit. It is considerably difficult to obtain amorphous thin films of ZnO and In_2O_3 by themselves. In the In_2O_3-ZnO solid solution system, high mobility of 40 cm^2/Vs or higher can be obtained, but it is difficult to reduce the carrier concentration. It is presumed Hosono et al. did not adopt that material for TFT for the reason that the high carrier density causes a degenerate state and results in a high off-current. As an exploratory method, they proceeded with research using the approach of doping Ga_2O_3 into the In_2O_3-ZnO system. By understanding Ga doping inhibit carriers, it is thought that the first candidate material for TFTs has settled around $InGaZnO_4$ with In:Ga=1:1. The process of arriving at this compositional system is an extremely important procedure for researchers searching for materials. In other words, the results of a series of basic crystallographic studies of homologous phases by Kimizuka et al. of NIRIM[3)-7)] described in Chapter 2, the evaluation of electrical conductivity of $In_2O_3(ZnO)_m$-$Ga_2O_3(ZnO)_m$ solid solution system in collaboration with Moriga of Tokushima University and Poeppelmeier of Northwestern University[8)], and the research on $InGaZnO_4$ crystals as a new transparent conductive oxide by Masahiro Orita et al.[20)] during the HOYA era. These three research results described above are all data on crystalline homologous conductive oxides. When we consider our search for non-crystalline amorphous oxide materials, it seems unreasonable to relate the approach of Hosono et al. to these three research results. Regardless of these three studies, the author believes their search route for amorphous oxide semiconductors led Hosono et al. to a material called $InGaZnO_4$ with an In:Ga:Zn = 1:1:1 composition. The results of the search in this triangular phase diagram are shown in Fig. 5.4. The details are documented in several papers[38)-41)] since the publication of the *Nature* article. The same details regarding the material search here are also described in the Project Research Completion Reports[42)] of ERATO-SORST, the successor project to JST's ERATO. The

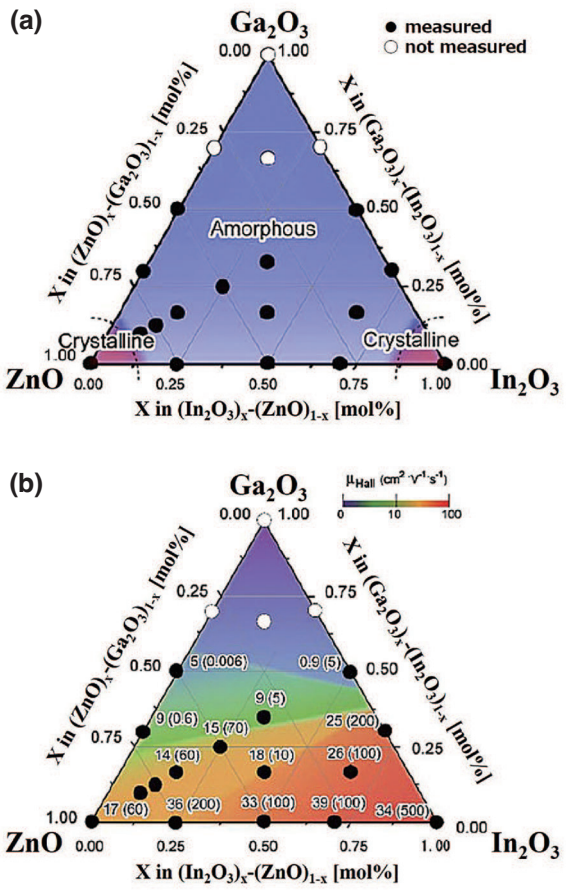

Fig. 5.4 Two triangular phase diagrams for In_2O_3-Ga_2O_3-ZnO system -from two viewpoints-
(a) Phase diagram for crystals and amorphous.
(b) Phase diagram of carrier concentration and electron mobility calculated from Hall measurements.
The number in parentheses means carrier density (unit: $10^{18}cm^{-3}$).
(Published two figures in reference (38) revised a little by courtesy of Prof. Hideo Hosono.)

concept and procedure of material exploration is a very important exploration process directly related to the discovery and invention of amorphous IGZO-based materials.

From a personal perspective, I will present a rationale from the viewpoint of homologous materials as to why choosing the oxide semiconductor $InGaZnO_4$ was the right choice. One reason supporting this composition was that for the $InGaO_3(ZnO)_m$ system, the amorphous phase is more easily obtained when $m < 4$. Additionally, a report[43] by Kenji Nomura in 2003 indicated that as the m value increases, the off-current might increase due to higher carrier concentrations. Consequently, $InGaZnO_4$ with $m = 1$ emerged as the material with the highest potential for minimizing off-currents. Furthermore, based on Moriga's evaluation of the correlation between the m value and the optical absorption edge[8], for the same In/Ga ratio, the bandgap increases as the m value approaches 1, and the transparent wavelength region extends toward shorter wavelengths in the visible range. From both the properties of homologous materials and the device characteristics reported by Nomura, the appropriateness of the $InGaZnO_4$ composition with a ratio of In:Ga:Zn = 1:1:1 becomes apparent. This is my perspective on the matter.

It may seem repetitive, but it is worth mentioning that the recent successful fabrication[34] of a junction with an amorphous pn hetero interface having steep diode characteristics near room temperature, using 2 types of amorphous oxide semiconductors, underscores the remaining device characteristics to be demonstrated in basic semiconductor devices are those of field-effect transistor properties using amorphous oxide semiconductors. The paper was published in *Nature* with meticulous preparation at the opportune moment and was the culmination of these efforts.

Silicon, a typical semiconductor, has strong, directional bonds. However, when silicon is transformed into an amorphous state, its electron mobility deteriorates significantly due to the disruption of electron orbital overlap, typically by 2 to 3 orders of magnitude compared to crystalline silicon. This deterioration means that the electron mobility in amorphous silicon is approximately 100 to 1000 times lower than in its crystalline form. Despite this inherent drawback, amorphous silicon thin film transistors (TFTs) have been widely adopted in liquid crystal displays (LCDs) from prioritizing the process advantage of enabling large-area thin films with high commercial value over the significant reduction in electron mobility. In this situation, Hosono presented a groundbreaking working hypothesis at the Sixteenth International Conference on Amorphous Semiconductors in 1995, challenging the conventional wisdom surrounding amorphous semiconductors[28]. The gist of the working hypothesis that Hosono presented at the conference was "For materials satisfying certain electronic configurations (utilizing the outermost s orbitals of heavy metal ions), the conduction band, which serves as the pathway for electrons, would be spatially more delocalized. When spherically symmetric s orbitals are the primary components of the conduction band, even in an amorphous state with disordered atomic arrangements, the overlap between s orbitals would be partially maintained, preventing a significant decrease in electron mobility".

The amorphous oxide semiconductor a-$InGaZnO_4$, used as the active layer in the Thin Film Transistors (TFTs) featured in *Nature*, was meticulously chosen based on the working hypothesis and extensive research achievements previously described. The electron mobility of this transparent amorphous IGZO-based oxide semiconductor was maintained at a surprisingly high value, exhibiting a mere one-order-of-magnitude reduction compared to its crystalline form. The experimental data demonstrated that the overlap of the s-orbitals of the metal ions, which are assumed to govern electrical conduction, is sufficiently maintained.

In stark contrast to what was published in *Science*, using an amorphous thin film rather than crystals for the transistor's semiconductor channel enabled a room-temperature thin-film deposition, typically fabricating under a low-temperature process. This opened up the possibility of utilizing a diverse range of substrates, including plastics. While the paper specifically mentioned polyethylene terephthalate (PET) as an example, the success of these amorphous oxide semiconductor TFTs effectively opened the door to flexible electronics. Moreover, the entire TFT device is transparent since transparent ITO material is used for the source, drain, and gate electrodes. This achievement marks a significant milestone in the evolution of transparent/transmissive electronics. The paper reported values between 6 and 9 cm^2/Vs for electron mobility. Mobilities of around 10 cm^2/Vs or higher are expected with further optimization, representing at least a tenfold improvement compared to amorphous silicon, significantly enhancing device performance.

The schematic diagram (left) and photograph (right) of a flexible transparent amorphous oxide thin-film transistor fabricated on a bendable polyethylene terephthalate (PET) sheet is shown in Fig. 5.5.

Once again, the author believes that the a-$InGaZnO_4$-based amorphous oxide semiconductor transistor technology published in *Nature* has the following notable features.

[I] Electron mobility at least one order of magnitude higher than that of amorphous Si-TFTs was achieved using the amorphous oxide semiconductor, a-$InGaZnO_4$. The fact that the decrease in electron mobility due to amorphization was less than expected confirmed that "Hosono's Working Hypothesis" was correct.

[II] The current on/off ratio of the TFT is 3 to 5 orders of magnitude, and the leakage current is extremely small. It is important to be able to operate as a transistor even when the carrier density in the semiconductor channel layer is quite low. The discovery of amorphous IGZO-based materials with the ability to operate at carrier densities of $10^{18}/cm^3$ or less is truly outstanding in terms of achieving on/off ratios of several orders of magnitude or suppressing off-current values to very low levels.

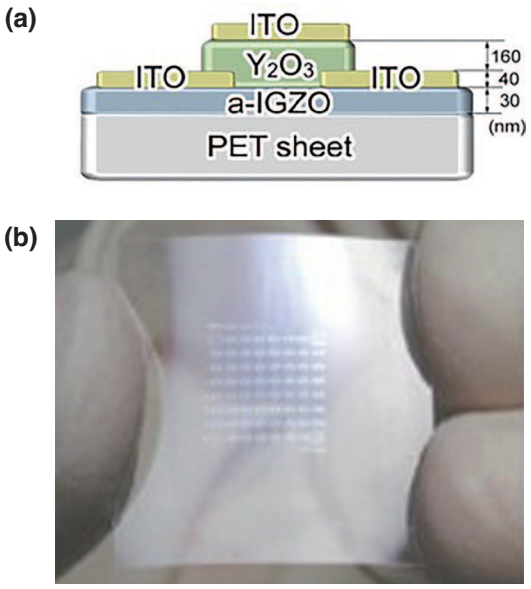

Fig. 5.5 Side-view image (a) and the photograph (b) of a flexible and transparent amorphous oxide thin film transistor fabricated on a bendable polyethylene terephthalate (PET) sheet.
The amorphous oxide semiconductor film (a-$InGaZnO_4$) formed on PET film works as the active layer in TFT. The gate insulator is Y_2O_3, and the source, drain, and gate electrodes are all ITO, transparent conductive oxides. As a result, an entire TFT becomes transparent.
This photograph of TFTs formed on PET film can be successfully taken by adjusting the angle of the TFT films. (These illustration and photographs are courtesy of Prof. Hideo Hosono.)

[III] This transistor can be fabricated using low-temperature processes, including room temperature.
The amorphous film remains stable in its amorphous state up to about 500ºC. This fact is a major advantage in the oxide transistor fabrication process because it greatly enhances the controllability of oxygen defects by oxygen partial pressure controlling.

[IV] Flexible devices can be realized by using various plastic materials as substrates. In other words, organic materials such as PET, polyethylene naphthalate (PEN), and polyimide can be used as substrates, which is of great industrial significance as it opens the door to flexible electronics.

[V] The fact that the entire TFT can be composed of transparent materials is also very significant because it has created a new value-added device called "transparent and transmissive electronics".

With such an attractive combination of features, it is easy to understand why this work garnered significant attention from researchers in the same specialized field worldwide and researchers and developers involved in the electronics industry worldwide. This *Nature* paper received an exceptionally high number of citations, with 6,198 citations according to Scopus and 8,026 citations on Google Scholar (as of October 5, 2022), providing clear evidence of the immense global attention it has received from researchers.

Eight years after its publication in *Nature* in 2012, a public technology report[44] by Sharp Corporation, a leading display manufacturer, featured a remarkable statement by Takuya Matsuo, a key figure in developing IGZO transistors at the company's Display Device Development Division. Matsuo declared, "The emergence of oxide semiconductors represents a major paradigm shift in the long history of silicon semiconductors, which has spanned over 50 years", highlighting the profound significance of the advent of oxide semiconductors.

Hideo Hosono made the decision to open the door to two unconventional trajectory routes. Opposite to the trends in epitaxial single-crystal oxide thin film technology, which is the main part of "oxide electronics", that were in the limelight at the time, furthermore, Hosono has also completely cut off the long-accumulated flow of technology related to homologous crystals and has set materials in the amorphous phase as the final form of materials and devices getting on the industrial stage. This is the first course correction. In addition, Hosono has switched to a material design policy of moderately suppressing carrier density, which also goes against the trend of developing transparent conductive oxides. This is the second course correction. Hosono implemented these two major course corrections [from crystal and higher carrier density to amorphous and controllability of carrier density] regarding material design with firm conviction. Looking back on these "**two noble course corrections**", which are insightful and directly focused on industrialization, today, the author feels that they were indeed a very wise decision. In the background of successful of this major course correction, it is thought that Hosono's strong enthusiasm and belief in "Essential for life" is, and his mind was conveyed to the main members, Masahiro Orita, Hiromichi Ohta, Kenji Nomura, and Toshio Kamiya, as well as by sufficient mutual communication within the JST-ERATO project. Of course, it was also due to the dedicated and extremely energetic efforts of the members themselves. In fact, in the website[45] of the Hosono Laboratory at that time states, "We started working on the application of amorphous oxide TFT about a year ago, and the idea of FET application by Kamiya, the TFT system proposal by Ohta, and the process optimization by Nomura were successfully brought together, leading to this achievement", which fully shows that the project team worked together to achieve the research object.

The author would like to commend the research results, which are truly outstanding and extremely high in originality, from the fundamentals of material design to the clarification of device properties that are of interest to industrial R&D researchers, on the basis of amorphous oxides, a field that has not been considered at all. In the current trend of oxide electronics, few researchers in the world have shown any interest in amorphous materials. The amorphous materials have long been associated with the image of "glass," but the fact that the company has completely dispelled this image and paved the way for amorphous oxide semiconductor materials as a new electronic material for the electronics industry is truly a

revolutionary achievement. This *Nature* paper of 2004 must be deeply engraved in the history of the two fields of materials science and semiconductor electronics as a "**great achievement**."

In assembling the JST ERATO project team, Hideo Hosono did not limit himself to personnel from the Tokyo Institute of Technology. Instead, he strategically selected researchers with the necessary expertise to tackle the material development challenges head-on, took on the difficult challenge, and continued to produce innovative research results in a short period of time. I would also like to pay tribute to Toshio Kamiya, Hiromichi Ohta, Kenji Nomura and Masahiro Orita, who have carried out and overcome the many high hurdles set by Hosono over the long period of time from ERATO to the successor project, ERATO-SORST, and Masahiro Hirano who always followed up on the whole project as a technical advisor. Each member's dedicated and diligent efforts deserve equal praise.

Today, we are in a transitional period where computer, television, and mobile phone displays are shifting from LCDs to organic light-emitting diodes (OLEDs). The valuation of the global market for TFT panels used in liquid crystal and OLED displays is estimated to be around 10 trillion yen. The discovery and invention of In-Ga-Zn-O-based TFTs by Hosono's group have spurred Japanese and international companies to accelerate commercialization, with the technology maturing and moving towards new stages of development. Amid this backdrop, it is presumed that there was significant demand for Hosono to share his insights. In July 2018, the "Reverse Engineering" column in *Nature Electronics* featured an article titled "How we made the IGZO transistor", in which Hosono recounted the development story of the IGZO-TFT[46), 47)]. This was an important page column in the history of transparent amorphous oxide semiconductor transistor technology.

Exactly ten years after the announcement of the working hypothesis for the exploration of transparent amorphous oxide semiconductors, in 2005, Hosono was invited to deliver a keynote speech at the International Conference on Amorphous Semiconductors held in Lisbon, Portugal, which had seemingly ignored him before. The invitation was undoubtedly a great honor for him. According to some reports[48), 49)], Hosono began his keynote presentation with the words: "This presentation is a kind of revenge". This phrase was a notably witty moment characteristic of Hosono.

In 2013, Hosono received the prestigious "Mott Lecture Award" from the International Conference on Amorphous Semiconductors. The award must have been a source of immense joy and pride for Hosono[50), 51)]. Furthermore, in March 2015, the Japan Academy recognized Hosono's achievements in "the creation and application of inorganic electronic functional materials" by bestowing upon him the Imperial Prize and Japan Academy Prize[52)]. In addition, Hosono received the prestigious Japan Prize in 2016[53)]. This award was established in 1985 and is presented to individuals whose original and outstanding achievements have advanced the development of science and technology, contributing significantly to the peace and prosperity of humanity worldwide.

Recently, in 2020, the journal Matter, published by Cell Press, featured a scientific commentary[54)] titled "The Holey Grail of Transparent Electronics". In this article, the authors cited Hosono's working hypothesis paper[28)] and a review[55)] by Kawazoe, stating, "The group led by Hideo Hosono should be credited for articulating many transparent conductor design principles that we now take for granted". In other words, the passage states that "The series of research results by Hideo Hosono's group should be more highly evaluated because they clearly demonstrated the design principles of transparent conducting oxides and transparent oxide semiconductors that are now commonly used."

This acknowledgment reflects the global research community's high regard for Hosono's group for their fundamental contributions to the design principles and material creation strategies for amorphous transparent IGZO and p-type oxide semiconductors. Undoubtedly, the publications in *Science* in 2003 and *Nature* in 2004 marked significant milestones that have since influenced numerous researchers and developers in materials and device technologies, serving as the genesis of new technological trends.

In 2022, Hideo Hosono published a comprehensive book on IGZO transparent oxide semiconductor materials and thin film transistors through Wiley[56)]. The title of the book is follows.

"Amorphous Oxide Semiconductors: IGZO and Related Materials for Display and Memory".

This book incorporates the latest research findings from global experts in transparent oxide semiconductor materials, thin film transistors, and their applications in displays, memories, and related technologies, providing access to more accurate and up-to-date technical information.

At the end of this chapter, I want to acknowledge the various sources of information, papers, and other materials I referred to while preparing this systematic survey report[57)-85)].

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53) Please refer to the following URL about The Japan Prize. (Viewed on 08.03.2022)
- Laureates of The Imperial and Japan Academy Prize
https://www.japanprize.jp/prize_prof_2016_hosono.html [in Japanese]
https://www.japanprize.jp/en/prize_prof_2016_hosono.html [in English]
- Achievements: Creation of unconventional inorganic materials with novel electronic functions based on nano-structure engineering
https://www.japan-acad.go.jp/pdf/youshi/105/hosono.pdf [in Japanese]
https://www.japan-acad.go.jp/pdf/youshi/105en/hosono.pdf [in English]
https://www.japanprize.jp/data/prize/2016/j_1_achievements.pdf [in Japanese]
https://www.japanprize.jp/data/prize/2016/e_1_achievements.pdf [in English]
- Professor Hideo Hosono receives the 2016 Japan Prize
https://www.titech.ac.jp/news/2016/033298 [in Japanese]
https://www.titech.ac.jp/english/news/2016/033481 [in English]
- Professor Hosono receives 2016 Japan Prize, gives a commemorative lecture
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• Hajime Shirai and Kenji Ueno: "Solution-processed Graphene Oxide as a Possible Material for Photovoltaic Device", pp. 215-221.
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• Atsushi Tsukazaki, Yusuke Kozuka and Masashi Kawasaki: "Recent Development in ZnO Related Heterostructures Towards Optical and Electrical Applications", pp.227-232.
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• ERATO "HOSONO Transparent ElectroActive Materials" Project
Research Director: Dr. Hideo Hosono (Professor, Materials and Structures Laboratory, Tokyo Institute of Technology)
Research Term: Oct. 1999 ~ Sep. 2004
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https://www.jst.go.jp/erato/en/research_area/completed/htd_P.html [in English]
(Viewed on 10.05.2022)
• ERATO "HOSONO Transparent ElectroActive Materials" Project Research Completion Report (JST Project Database)
https://projectdb.jst.go.jp/file/JST-PROJECT-7700000065/JST_1113100_7700000065_2004_%E7%B4%B0%E9%87%8E_PER.pdf [in Japanese]
(Viewed on 10.05.2022)

- ERATO “HOSONO Transparent ElectroActive Materials” Project Research Results
  https://www.jst.go.jp/erato/research_area/completed/htd_pj/results_1999-2004_hosono.pdf
  [in Japanese] (Viewed on 10.05.2022)
- List of academic papers, reviews, presentations, etc. of ERATO “HOSONO Transparent ElectroActive Materials” Project (as of September 30, 2004)
  https://www.jst.go.jp/erato/research_area/completed/htd_pj/publications_1999-2004_hosono.pdf [in Japanese] (Viewed on 10.05.2022)
- Japan Science and Technology Agency (JST) Strategic Basic Research Programs
  ERATO “HOSONO Transparent ElectroActive Materials” Project (1999-2004)
  Survey report on research development several years after project completion:
  https://www.jst.go.jp/erato/evaluation/follow/follow1999_hosono_shiryo.pdf [in Japanese]
  (Viewed on 10.05.2022)

6 Activities for Intellectual Property

6.1 Registered Patents

The Hosono Group is active in patenting intellectual properties (hereinafter abbreviated as IP). As 18 years have already passed since the announcement of IGZO-based transparent oxide semiconductors, this systematic survey reports on the author's own opinions and speculations based on the current status of registered patents.

Before the Hosono Group invented IGZO-based transparent oxide semiconductor, Masahiro Orita et al. of HOYA Corporation (hereinafter abbreviated as HOYA) had published research papers[1), 2)] on a new transparent conducting oxide, $InGaZnO_4$ crystal, and HOYA, a private company, had applied for and registered 4 patents related to the research papers. The four patents are Patent No. 3947575, Patent No. 3644647, Patent No. 3881407, and Patent No. 3945887.

As mentioned in Chapter 2, "conductive oxides" and "oxide semiconductors" are materials with completely different physical functions. These 4 registered patents were basic materials patents related to IGZO-based conductive oxide crystals or thin films thereof, with an octahedral structure of InO_6 or with claimed high carrier density.

Then, before the launch of the ERATO project, Hosono started joint research with HOYA in July 1998; about 1 year before the start of the ERATO project, Hosono and HOYA researchers jointly filed an important basic patent on amorphous conductive oxides and subsequently registered the patent as Patent No. 4170454, which was held for 20 years, the longest period that a patent can be maintained. This patent specification does not mention transistors, presumably because the patent was filed before the start of ERATO. At this point, neither Hosono nor HOYA had conceived the idea of applying the amorphous conductive oxide to the channel layer of transistors, and the conductive oxide may have been simply positioned as a promising candidate for a conductive oxide material to replace ITO.

Subsequently, when the ERATO project was launched, Hosono invited two researchers of HOYA, Masahiro Orita and Hiromichi Ohta, as key project researchers. Since then, for research outcomes of a series of projects, including ERATO and its successor ERATO-SORST, in most cases, important technical terms such as "(field-effect) thin-film transistor" or "amorphous" are clearly stated in the genus claim of the specification for basic patents on the world's first "IGZO-TFT" filed by Professor Hosono and his group at the Tokyo Institute of Technology.

From the list of Japanese registered patents in Table 6.1, Hideo Hosono's basic invention related to "a-IGZO TFT" was filed on March 12, 2004 (priority date). The three patents registered on this day are Patent No. 4568828 (In-Ga-Zn-O-based transparent amorphous oxide thin-film and thin-film transistor), Patent No. 4568827 (vapor-phase deposition method for In-Ga-Zn-O-based transparent amorphous oxide thin-film), and Patent No. 4620046 (In-Zn-based, In-Sn-based, In-(Zn, Sn)-based amorphous oxide thin-film transistor).

As shown in Table 6.1, Hosono holds over 20 patents registered solely in Japan. As of August 2022, he retains the

Table 6.1 A group of registered patents related to IGZO-based transparent oxide semiconductor transistors, of which Hideo Hosono is one of the inventors.
(Left side: Japanese registered patents, right side: U.S. registered patents.)

Japanese Resistered Patents checked on Jun. 25, 2022	US Resistered Patents checked on Jun. 5, 2022
Japanese Patent No. 4170454 (Filing date: Jul. 24, 1998)	US Patent 7,061,014 (Filed: October 31, 2002)
Japanese Patent No. 4298194 (Filing date: Nov. 5, 2001)	US Patent 7,453,065 (Filed: November 9, 2005)
Japanese Patent No. 4164562 (Filing date: Sep. 11, 2002)	US Patent 7,535,010 (Filed: November 8, 2007)
Japanese Patent No. 4620046 (Filing date: Feb. 28, 2005／Priority date: Mar. 12, 2004／Priority date: Nov. 10, 2004)	US Patent 7,601,984 (Filed: November 9, 2005)
Japanese Patent No. 5118810 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,663,116 (Filed: February 10, 2009)
Japanese Patent No. 5126729 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,791,072 (Filed: November 9, 2005)
Japanese Patent No. 5138163 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,829,444 (Filed: November 9, 2005)
Japanese Patent No. 5126730 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,863,611 (Filed: November 9, 2005)
Japanese Patent No. 5053537 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,868,326 (Filed: November 9, 2005)
Japanese Patent No. 5118812 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 7,872,259 (Filed: November 9, 2005)
Japanese Patent No. 5118811 (Filing date: Nov. 9, 2005／Priority date: Nov. 10, 2004)	US Patent 8,084,743 (Filed: June 30, 2008)
Japanese Patent No. 4568827 (Filing date: Mar. 24, 2010／Priority date: Mar. 12, 2004／Priority date: Nov. 10, 2004)	US Patent 8,168,974 (Filed: September 15, 2010)
Japanese Patent No. 4568828 (Filing date: Mar. 24, 2010／Priority date: Mar. 12, 2004／Priority date: Nov. 10, 2004)	US Patent 8,203,146 (Filed: September 15, 2010)
Japanese Patent No. 5168599 (Filing date: Mar. 31, 2010)	US Patent 8,212,252 (Filed: September 15, 2010)
Japanese Patent No. 5337849 (Filing date: Jul. 15, 2011／Priority date: Nov. 10, 2004)	US Patent 8,237,166 (Filed: August 2, 2010)
Japanese Patent No. 5401571 (Filing date: Jul. 15, 2012／Priority date: Nov. 10, 2004)	US Patent 9,130,049 (Filed: June 20, 2013)
Japanese Patent No. 5401570 (Filing date: Mar. 9, 2012／Priority date: Nov. 10, 2004)	US Patent 9,269,826 (Filed: January 5, 2011)
Japanese Patent No. 5451801 (Filing date: Mar. 15, 2012／Priority date: Nov. 10, 2004)	US Patent 9,583,637 (Filed: July 22, 2015)
Japanese Patent No. 5401572 (Filing date: Mar. 15, 2012／Priority date: Nov. 10, 2004)	US Patent 9,947,803 (Filed: April 29, 2011)
Japanese Patent No. 5401573 (Filing date: Mar. 15, 2012／Priority date: Nov. 10, 2004)	US Patent 10,032,930 (Filed: July 16, 2009)
Japanese Patent No. 5589030 (Filing date: Jul. 2, 2012／Priority date: Nov. 10, 2004)	US Patent 10,032,931 (Filed: September 23, 2011)
Japanese Patent No. 5946130 (Filing date: Jul. 3, 2012)	US Patent 10,615,287 (Filed: January 10, 2017)
	US Patent 11,075,303 (Filed: August 30, 2018)

rights to most of these patents. The same applies to overseas patents held by Hosono. Today, more than 20 patents for Hosono's invention have been granted as U.S. patents (including divisional patent applications). Refer to Table 6-1 (right side column)

I imagine that to lead such a large number of university-initiated applications to registration, experts with sufficient knowledge of patents must have always been around Hosono's project, working together as a team. In other words, there must have been capable brains around. The survey revealed that Yoshiyuki Nishi, a patent attorney, had handled more than 50 of Hosono's patent cases in total, consistently over 15 years, starting with a patent application related to optical holograms filed in 2000 at the early stages of ERATO, followed by patent applications for oxide-based pn junction diodes, IGZO-based transparent amorphous oxide semiconductor thin film transistors, electrides, which appeared as a new material, and iron-based superconductors, up until 2015 when a patent application was filed for transition-metal pnictide compounds. I imagine that Yoshiyuki Nishi and Hosono considered highly capable individuals, worked together for over 15 years in a mutually trusting relationship with the common goal of patenting many innovative functional materials. It is assumed that full-scale IP activities began after the summer of 2003, anticipating the publication date in *Nature*, to complete the filing of important patent applications before that date. The schedule for the start of full-scale IP activities is estimated to be about 6 months from before the filing of the basic patents in March 2004, and considering that the paper on crystalline IGZO-TFT was published in *Science* on May 23, 2003, it is likely that the preparation was started even earlier.

Around mid-March 2004, Hosono of Tokyo Tech considered that collaboration with companies would be essential for future development, including patents, and consulted with Isamu Shimizu, then Director of Tokyo Tech TLO (a professor at Tokyo Tech and one of the pioneers of amorphous silicon research at that time). Two months later, a meeting was set up with Canon Inc. (hereinafter abbreviated as Canon) through TLO in May. During that meeting, Hideya Kumomi, the leader of the Canon Research Center, said he had an intuition about the emergence of a new amorphous oxide semiconductor to replace amorphous silicon[3]. Tokyo Tech and Canon began joint research in September of the same year[3], after the win-win relationship between the two parties was mutually confirmed, with Tokyo Tech's desire to focus on academic creativity research and Canon's desire to take advantage of its corporate experience in device application technology, including the long-term corporate perspective. This joint research is completely separate from ERATO-SORST, the successor to ERATO.

Hideya Kumomi, a leader at Canon, worked together with Canon researchers and drew up a concept of the patent specification with a broad vision to include material technology for amorphous oxide semiconductors and also elemental devices such as diodes and thin film transistors, elemental circuits such as active matrices, and even component devices such as displays and sensors, as well as applied products, and based on this concept, restructured the patent specification in a short period to maintain an advantage in the market in the future[3]. Although Canon's support was actually to start in September, since there was a large bulk of work, and the time for publication of the paper in *Nature* was also approaching, Hosono was so careful that he adjusted the timing of his e-mail reply to the review comments on the submitted manuscript that he received from the office of the *Nature*, following the scheduled patent filing date. Since the publication in *Nature* was on November 25, 2004, it was necessary to apply for important patents before that date. In other words, it can be inferred that Hosono's group believed that this amorphous oxide semiconductor material technology had the potential to replace the stronghold of amorphous silicon. The priority date of November 10, 2004, stated in the specifications of many registered patents today, had the above tense background. In addition, due to the importance of the basic patent for Hosono's "IGZO-TFT", Kumomi and his team at Canon simultaneously considered overseas IP strategies and provided extremely important support[3] for the industrialization of amorphous oxide semiconductor transistors, including filing PCT applications and directly applying to Taiwan, which is not a member of the PCT Treaty.

In this way, the joint research with Canon has significantly contributed to patenting activities, with 14 registered patents in Japan filed jointly by Hosono (National University Corporation Tokyo Institute of Technology) and Canon. In particular, the mention of "field-effect transistor of amorphous oxide containing microcrystals" in the generic concept of the claims of the registered patents No. 5138163 and No. 5589030 is very significant from the perspective of patent strategy.

In the "International Intellectual Property Utilization Forum 2012" held on January 23, 2012, at Hotel Tokyo Nikko in Daiba, Minato-ku, Tokyo (hosted by the National Center for Industrial Property Information and Training), Hosono gave a special lecture titled "The Benefits and Pains of Intellectual Property for University Teachers: A Personal Experience". The content of that lecture was included in an article in Nikkei Crosstech under the heading "Strongly Aiming for Industrialization of New Materials, the Outcome of ERATO's Research and Development", which also describes the significance and importance of the joint research with Canon, as follows[4].

> "Tokyo Tech and Canon have promoted research and development for the application of TFTs made of amorphous oxide semiconductor IGZO. At this time, application and peripheral patents filed jointly by Tokyo Tech and Canon were also created into a patent pool, and licensing through technology transfer was entrusted to the Japan Science and Technology Agency. Professor Hosono said that even if universities produce original basic patents unless they conduct joint research with companies interested in the application and file many application and peripheral patents, industrialization is

difficult, and this is what I learned through joint research with companies."

As seen from the interview article above, Hosono and many university professors have the perception that "basic patents alone are sufficient". This viewpoint seems to have been the case in the early stages of the Hosono Project. However, the introduction of a strategic patent application approach by Canon, a private company, at the right time resulted in a systematic patent application for the Hosono Project. I believe this measure is a typical example of how introducing a private company's approach contributed significantly to the industrialization of "IGZO-TFT" technology.

Canon's participation was also a big plus from a technological perspective, as it helped strengthen the TFT device development. Hideya Kumomi, the leader at Canon, received the 19th (FY 2005) Advanced Technical Grand Award of Originality, Special Prize[5], along with key members of the Hosono Group, during the early stages of his participation. Since then, Kumomi et al. have continued to publish papers on IGZO-based amorphous oxide semiconductor thin-film transistor technology[6)-28)]. In particular, the paper by Yabuta et al.[6)] of Canon is the world's first paper on sputter deposition of amorphous a-IGZO semiconducting oxide thin film. It is noteworthy for its high number of citations.

It can be inferred that, thereafter, while having Yoshiyuki Nishi, the patent attorney mentioned above, Masashi Furukawa, who was then in the JST Special Project Promotion Office (later the Research Project Promotion Department) and has since strongly supported ERATO-SORST, ACCEL, and the Strategic Creative Research Promotion Business Area, and Masahiro Hirano, who was the technical advisor for the ERATO Project and has always played the role of liaison with Hosono, as the core members of the Hosono's patent strategy group. The activities toward mission accomplishment were carried out in an extremely functional manner to prepare for future patent licensing agreements and patent disputes by individually determining detailed assignments and adding high-quality members, including Masaru Ozaki, who has extensive experience in the private sector, and Yuichiro Takahashi, an attorney and patent attorney from Takahashi Yuichiro Law Office, and others[29), 30)].

As a result, patents related to IGZO oxide semiconductor transistors by the Hosono Group are now registered in various countries around the world, including Europe, South Korea, China, Taiwan, Australia, India, Canada, Brazil, and Russia, as shown in Fig. 6.1.

6.2 Patent Licensing

On July 20, 2011, JST (Chairman: Koichi Kitazawa), the patent holder of "IGZO-TFT", signed a licensing agreement with Samsung Electronics Co., Ltd. (President and CEO: Choi Gee-sung) for patents related to the high-performance IGZO-based thin-film transistor technology invented by Hosono et al.[31)]. The licensing agreement with Samsung is the first with a private company, in Japan and overseas.

Subsequently, on January 20, 2012, JST entered into a licensing agreement with Sharp Corporation (hereinafter abbreviated as Sharp), a major Japanese company, for Hosono's

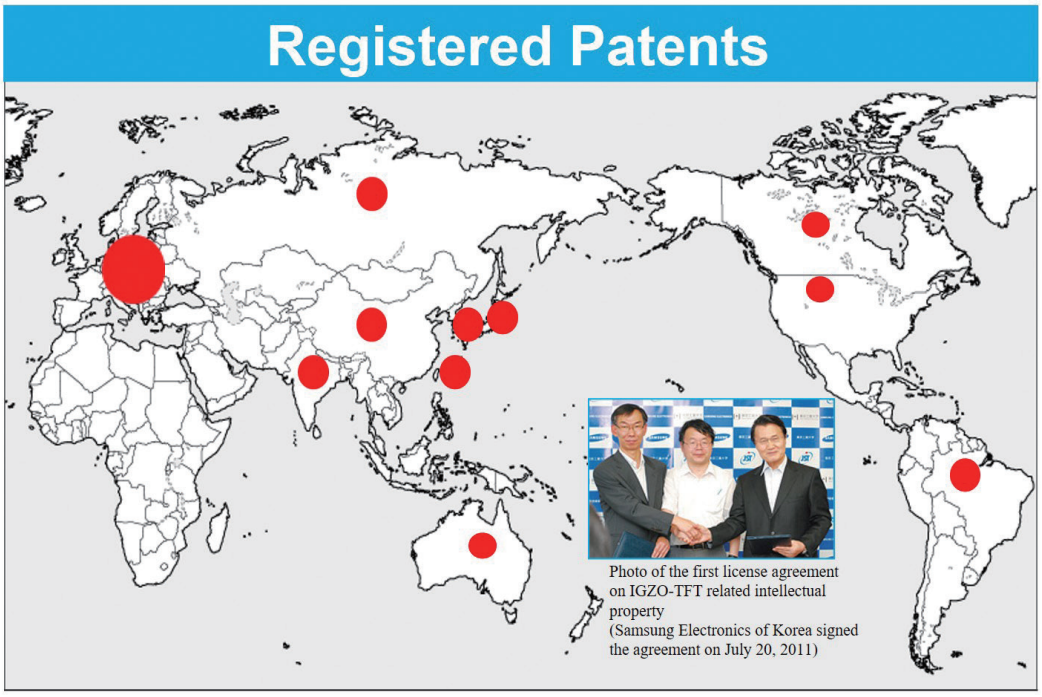

Fig. 6. 1 Image showing that the patent for IGZO-TFT by Hideo Hosono et al. has been registered in many countries around the world.
(This image was received and published courtesy of Prof. Hideo Hosono. (2022.05.04)
The inset photo in the map was taken at the time of the licensing agreement with Samsung Electronics Korea.)

oxide semiconductor transistor technology[32].

However, the licensing agreement with Sharp was made public only on May 29, about four months after the agreement was signed. Why was the announcement delayed for so long? I guess that it was a "non-disclosure matter for the time being" agreed upon by both parties, but the author cannot think of any reason for JST to delay the announcement and imagines that Sharp must have had their reasons. One of the grounds for such imagination is the content published by Sharp on April 13 of the same year[33]. Some excerpts from the news release article are reproduced below.

> "We are the first company in the world to begin production of high-performance LCD panels that use oxide semiconductors (IGZO)* at our Kameyama Plant No. 2 in March, and we will start full-scale production in April. *Joint development of thin film transistors using oxide semiconductors (IGZO) with Semiconductor Energy Laboratory, Co., Ltd (Head office: Atsugi-shi, Kanagawa, President: Shunpei Yamazaki)"

This sentence could be taken to mean that Sharp has an agreement to license IGZO from JST on the one hand, but on the other hand, Sharp is manufacturing and producing IGZO using "another IGZO" being developed at Semiconductor Energy Laboratory, Inc. (hereinafter abbreviated to SEL for brevity). JST, which had already concluded a patent license agreement, may have seen this announcement from Sharp as a puzzling or concerning news release.

It is inferred that JST and Sharp held another round of discussions due to concerns that the above misunderstanding and misperception might arise. It is imagined that, as a result, it was announced[34] on May 29 that "The patent license agreement had already been concluded on January 20". Excerpts from the announcement made at that time are shown below.

> "On January 20 this year, Sharp concluded a licensing agreement with the Japan Science and Technology Agency (Chairman: Michiharu Nakamura, hereinafter referred to as JST) for patents related to thin film transistors using oxide semiconductors (IGZO). As our company has started full-scale production of LCD panels using IGZO, we are pleased to announce this matter based on an agreement with JST. The patent was invented by Professor Hideo Hosono of the Tokyo Institute of Technology (President: Kenichi Iga) and others as part of JST's Creative Science and Technology Promotion Project and consists of dozens of patents, including applications filed by the Tokyo Institute of Technology and others, which are licensed collectively by JST. In 2004, Professor Hosono and his colleagues found that when used in thin film transistors, the electron mobility is one order of magnitude higher than that of amorphous silicon used in conventional LCD panels. The outcome was published in the science journal *Nature* in November of the same year. Sharp has jointly developed high-performance LCD panels using this IGZO with Semiconductor Energy Laboratory, Co., Ltd (Head office: Atsugi-shi, Kanagawa, President: Shunpei Yamazaki). The production of these panels began at the Kameyama Plant No. 2 in March, and full-scale production started in April. Since the panels have high resolution and consume less power, they will be supplied for a wide range of applications such as mobile devices, high-definition notebook PCs, and high-definition LCD monitors, thereby contributing to the creation of new product markets."

From this new announcement, it was clear that (1) The patent for which Sharp signed the licensing agreement was invented by Professor Hideo Hosono and his group at the Tokyo Institute of Technology under JST's Creative Science and Technology Promotion Project (ERATO). (2) Sharp will adopt Hosono's IGZO technology to jointly develop high-performance LCD panels with Semiconductor Energy Laboratory, Co., Ltd. Thus, the flow of events (distinction between upstream and downstream) between these two matters became very clear. From the standpoint of the reader of this news release, it is the author's impression that the text has been restated in a way that makes the order of things make sense quite neatly.

However, following this immediately on June 1, Sharp announced a new IGZO-based material in collaboration with SEL[35]. The main points of the content are given below as excerpts.

> "Our company and Semiconductor Energy Laboratory, Co., Ltd have jointly developed a new technology for highly crystalline oxide semiconductors (IGZO). ~Omitted~ This jointly developed IGZO is an oxide semiconductor composed of In (indium), Ga (gallium), and Zn (zinc), to which crystallinity has been added. Compared to the current IGZO, it is possible to achieve further miniaturization and higher performance of thin film transistors, and the material is expected to be adopted in liquid crystal displays for mobile devices such as smartphones, which are becoming increasingly high-definition. Furthermore, it can also be applied to OLED displays."

In addition, the following was added as a supplement to the same news release:

> "Sharp Corporation and Semiconductor Energy Laboratory, Co., Ltd have discovered a new crystal structure in the development of oxide semiconductors. Both the companies named this crystal structure CAAC (C-Axis Aligned Crystal)."

The content of this news release from Sharp on June 1, as understood by the author, is that Sharp and SEL jointly developed a new technology for completely different, oriented crystalline IGZO-based-oxide semiconductors that can achieve further miniaturization and higher performance compared to the IGZO-based amorphous oxide semiconductor developed by Hosono et al. If so, the intention of the licensing agreement signed with JST, announced a few days ago, could be based on the prior judgment that "it would be difficult to progress to commercialization with SEL's technology alone", due to which it was decided to obtain a patent license for the

basic patent group of "IGZO-TFT" owned by JST as soon as possible. But the truth is beyond imagination. This situation must have been a very uneasy case from the standpoint of the intellectual property personnel at JST, an independent administrative agency at the time, because the party with whom they signed the licensing agreement was one of the world's leading private Japanese companies.

It is difficult for an outsider like the author to comment on this, as even very small matters in a company's patent strategy can significantly affect the business. However, looking back at the series of news releases in 2012 from today's perspective, more than 10 years later, one can understand how the IGZO-TFT technology was recognized as an important technology in the display field, and at the same time, one can clearly understand the respective positions of the three parties, namely, JST, the world's leading display manufacturer Sharp, and SEL concerning the IGZO-TFT technology, and it is deeply moving to get a glimpse of the reality of research and development in the early days of oxide semiconductor transistors.

I would like to briefly touch on developments regarding patent licensing agreements for thin-film transistor technology. To the best of the author's knowledge, JST, unfortunately, has not yet released information on how many licenses have been granted to companies in various industries worldwide. However, based on the author's long experience researching functional oxide thin films, it seems that licensing patents to target manufacturers for thin film fabrication begins at an early stage. Otherwise, it would be impossible to fabricate thin film transistors for producing displays. In fact, in 2010, JX Nippon Mining & Metals Corporation (now JX Advanced Metals Corporation) succeeded in mass producing a large sputtering target of 2.7 meters in length for the first time, ahead of other companies, and Hosono and President Oi of JX Nippon Mining & Metals Corporation received the 40th Harunari Inoue Award in July 2015[36]. In his acceptance speech, Hosono said,

> "JX Nippon Mining & Metals Corporation, which is jointly receiving the award, was the first to perfect the technology, and in 2010, they exhibited the actual product at an international workshop (TAOS 2010) hosted by Tokyo Tech. This information conveyed to the participants that preparations for commercialization were in progress. JX Nippon Mining & Metals Corporation was the first company to receive a patent license and successfully commercialize the product. Since then, many Japanese and international companies have followed suit. I would like to express my respect for the company's high technical capabilities and morals."

He also confided that the patent licensing agreement with JX Nippon Mining & Metals Corporation was the quickest. In addition, since there are many material manufacturers in Japan, the author believes that the total number of licensing agreements may be about 10, including those with overseas target manufacturers.

A 2013 review paper[37] by Toshio Kamiya, who was active in the Hosono Group and is currently a professor, provides a detailed description of large sputtering equipment and its large targets. As a reference image, a photograph showing the size of the target for the sputtering equipment at the time is shown in Fig. 6.2.

Fig. 6.2 Targets for large deposition systems
(This photograph was by courtesy of Dr. Masashi Furukawa (Japan Science and Technology Agency: JST).)

On the other hand, many display manufacturers often produce TFTs in-house. It is imagined that the patents have been licensed to major Japanese and foreign display companies and LCD panel manufacturing companies, including the above-mentioned Samsung Korea and Sharp. If information on the kind of companies around the world with whom licensing agreements have been signed for the Hosono Group's "IGZO-TFT" patent is disclosed more accurately, it will provide positive feedback to the young researchers who will lead the next generation, as a good concrete example of how basic research at universities has greatly contributed to industrialization, which will be a good stimulus for them to return the benefits.

6.3 Efforts to Protect University-Originated Intellectual Properties from an Industrialization Perspective

Many people are probably familiar with Hosono's habit of saying, "Materials research is not only for academic purposes and is genuine only when its results are useful to the industry." The incident that symbolizes his meaning was an appeal against an examiner's decision of refusal at a trial court of the Korean Patent Office. In the second half of this section, we will touch on these contents in as much detail as possible.

First, I will introduce some excerpts from an interview[38] with Hosono published in the 2013 issue of the Journal of

Industry-Academia-Government Collaboration.

"This technology has already led to commercialization, and a fierce battle is unfolding between companies and related organizations, including over patents. However, it is incorrect when some newspapers reported that 'a groundbreaking semiconductor patent was granted to Samsung in advance'. Behind the scenes was our patent trial in South Korea, and since we won that trial, we officially licensed the patent to Samsung. We just issued a general license with no restrictions, and our first agreement just happened to be with Samsung. It was not a case of preferential treatment. Currently, we are giving patents to LG, Japanese companies such as Sharp, and Chinese companies. Our IGZO is a typical example where 'companies were forced to use the material'. Basically, no one wanted to use IGZO. Everyone thought semiconductors were made of silicon, and there was resistance to using a dirty material like oxide. Despite this, companies were forced to use IGZO for a simple reason, i.e., no matter who tried it, the material delivered 20 times the performance of amorphous silicon. I am not saying it was good or bad, companies had to use the material. It quickly became popular since the material was good and easy to make."

In this way, the detailed history of licensing the early IGZO transistor patents and the background to the spread of commercialization described through Hosono's eyes are very interesting.

In recognition of his efforts in this series of intellectual property activities, Hosono received the Excellence Award of the 12th Japan Innovators Award[39] (sponsored by Nikkei BP) in October 2013. This award is given to people who have opened up new markets with original ideas, and the Excellence Award was given to Professor Hosono in appreciation of the fact that the IGZO-based thin-film transistor technology developed by Hosono et al. was put into practical use as a new flat-panel display by major companies, backed by substantial intellectual property rights. In the news release is a comment from Hosono expressing his gratitude to the project members, the excerpts of which are given below.

"This research is one of the outcomes of JST's ERATO and ERATO-SORST projects. I want to thank Dr. Kenji Nomura (currently Associate Professor at the University of California, San Diego) and Dr. Toshio Kamiya (currently Professor at the Laboratory of Frontier Materials), the researchers at Canon with whom we conducted joint research in the early stages of the project, and the people at the JST Intellectual Property Center for their help regarding patents." (*As the current affiliations of Dr. Nomura and Dr. Kamiya have changed from those at the time of the news release, their affiliations have been revised to those as of August 2022.)

Furthermore, on February 25, 2015, Hosono was awarded the Intellectual Property Special Contribution Award by JST, which is given to outstanding researchers who have contributed to the development of science and technology in Japan by creating and utilizing intellectual property based on original research outcomes[40]. Fig 6.3 shows a group photograph of those involved during the award ceremony.

Fig 6.3 A photograph[44] of Prof. Hideo Hosono, winner of the JST Intellectual Property Special Contribution Award, with his colleagues who made significant contributions to his IP activities
(Titles omitted: from left to right: Masaru Ozaki (JST), Yoshio Namba (JST), Yoshiyuki Nishi (Patent Attorney), Hideo Hosono (Professor), Masashi Furukawa (JST), Masaharu Kubo (JST), Shinichiro Miki (JST).)[30]

This Intellectual Property Special Contribution Award was established in 2011, and the first recipient was Isamu Akasaki, a tenured professor at Meijo University, who developed the blue light-emitting diode and was awarded the Nobel Prize in Physics in 2014. Hosono was the second recipient of this award. In a news release by the Tokyo Institute of Technology, Hosono commented on intellectual property rights and expressed his gratitude for the efforts of all the researchers around him[40].

"Based on the design guidelines for high mobility amorphous oxide semiconductors (TAOS) that were first presented at the 16th International Conference on Amorphous Semiconductors in 1995, research was conducted on the application of TFTs thereof in the JST ERATO "Transparent ElectroActive Materials Project" started in 1999, the outcomes of which were published as papers (in Science and Nature) and intellectual property rights were obtained. I am happy that the papers and the patents have been cited more than 5,000 times and have led to practical applications. Research on oxide TFTs, such as IGZO, which has high mobility, was initiated with the assumption that it would be used to drive OLEDs, and it looks like it's finally being used here. I express my deep gratitude to our collaborators, including Dr. Kenji Nomura (currently at Qualcomm), Dr. Toshio Kamiya (Tokyo Institute of Technology), Dr. Masahiro Hirano (formerly at JST), Dr. Hiromichi Ohta (currently at Hokkaido University), and Dr. Masahiro Orita (formerly at Hoya). I would also like to express my gratitude to the relevant parties at Canon, who were introduced by the late Professor Isamu

Shimizu (then Director of Tokyo Tech TLO), with whom I was able to carry out useful joint research."

On July 17, 2019, JST published the following notice on its website: "To All Companies Considering Research, Development, and Commercialization of "IGZO-based oxide semiconductor TFTs", and To All Parties Interested in the 'IGZO trademark'"[41]. Important information from the notice regarding intellectual property rights for amorphous IGZO-based oxide semiconductor transistors is summarized below.

"The originality of 'IGZO-based oxide semiconductor TFTs' has been technically and academically attributed to Professor Hideo Hosono of the Tokyo Institute of Technology (currently Honorary Professor at the Tokyo Institute of Technology and Director of the Materials Research Center for Element Strategy), who led 'HOSONO Transparent ElectroActive Materials' under JST's Creative Science and Technology Promotion Project (ERATO), and his group. The patents for 'IGZO-based oxide semiconductor TFTs' currently licensed by JST include a package of patents for thin films, whether the active layer in the TFT is monocrystalline, polycrystalline, microcrystalline, or amorphous, and peripheral patents. JST collectively licenses the relevant patents to companies, etc. Major patents, such as basic patents included in the group of patents, are registered with the rights maintained in Japan, South Korea, Taiwan, Europe, the United States, China, etc., and are licensed for non-exclusive use. Hence, these patents can now be licensed to companies considering using IGZO-based oxide semiconductor TFTs for displays, memory, etc. ~Omitted~ In addition, since around 2014, Semiconductor Energy Laboratory Co., Ltd. has been filing lawsuits against rights holders such as JST, challenging the validity of some of the patents included in this group of patents by filing invalidation trials and oppositions in Japan, South Korea, Taiwan and Europe. However, the validity of these patents has been confirmed in all the countries, and as of April 13, 2019, all cases are closed."

Thus, through the notification from JST, Hosono's patents are considered to be held almost intact today, as described in the original specification as registered, without any modification.

I have some thoughts to share regarding the above description of "IGZO patents" on JST's website. When I think of the hardships that university professors and researchers in Japan have had to face when directly asserting and defending the validity of their basic patented inventions before patent offices and courts, both in Japan and overseas, over 5 years of relentless patent invalidation challenges, all the while engaging in new research, administering universities, and guiding their students, the establishment of a support system that will allow universities to receive stronger support from JST and intellectual property-related departments in universities when applying for and holding patents in the future seems necessary.

JST made a similar announcement regarding intellectual property on June 11, 2019, in the notice "Initiatives for the Protection and Utilization of Intellectual Property Rights Concerning Research Results"[42]. Furthermore, this was also discussed in a news release article (June 20, 2019) titled "IGZO Patent Lawsuit Settled; Professor Hideo Hosono's Invention Approved"[43]. An interview with Prof. Hideo Hosono by Yasuhiro Yamaguchi, editor-in-chief of the Journal of Industry-Academia-Government Collaboration, published by JST in November 2019, also includes insights on the various challenges in maintaining rights[44]. I think some statements are particularly important, the excerpts of which are given below.

"You will not appreciate the value of patents unless you file one yourself. I also realized it would be futile if the inventors were not involved in patent disputes. A high degree of originality is required in the academic field, and losing a dispute over intellectual property would set a bad precedent for academia. My case took 6 years to conclude. ~Omitted~ I put pressure on myself, thinking that while papers are important for researchers, they are not the be-all and end-all, and we must also create something that will prove useful to the world. So, I spoke with companies dealing with displays in Japan, but they did not understand me at the time. The company that showed the most enthusiasm and the first to contact me was Samsung."

This means that while most Japanese companies stood on the sidelines, a firm from neighboring South Korea perceived the essence of Hosono's completely new amorphous oxide semiconductor material technology. The harsh reality of the decline in electronics technology in Japan, which once claimed to be a semiconductor powerhouse, was brought to the fore in such situations. This situation must have saddened Hosono himself more than anyone else.

Hosono delivered an address[4] at the "International Intellectual Property Protection Forum 2012" mentioned above, leaving quite an impression with his attitude and response when appealing against the decision of refusal issued by the Korean Intellectual Property Office. His lecture is reproduced below.

"One of the highlights of Professor Hosono's special lecture was his response to the Korean Intellectual Property Office's denial of the uniqueness of the basic patent he filed on the grounds that the invention was 'easy to assume'. The patent had been granted in Japan. However, the Korean Intellectual Property Office decided to reject his patent application. This incident took place in May 2009. Professor Hosono was surprised to learn that even internationally recognized original research results at academic conferences are not necessarily recognized in the patent world. Reacting to the denial of a patent for his research findings, acknowledged as innovative in the academic community, he expressed, 'I felt as though my 5 years of research efforts were being rejected, so I

focused my energies to securing the patent.' Typically, examiners at the Japan Patent Office assess the novelty and originality of patents based on the principle of literature. For this reason, Professor Hosono acted as the 'supporting counsel' to the patent attorney representing the patent applicant JST in contesting the refusal decision issued by the Korean Intellectual Property Office. 'II felt that it is important for the researchers themselves to explain the novelty of their research results carefully', he said of this experience, and continued, 'It is my opinion that patent disputes cannot be won unless inventors seriously work toward obtaining patents.'"

This appeal against the denial decision in South Korea could go ahead after Hosono consulted with JST Chairman Koichi Kitazawa and received the generous support of Chairman Kitazawa and advice from Canon[45], as can be gleaned from the following information[46]. An excerpt from Hosono's more straightforward statements is presented below.

"When we filed an international patent application for the transparent amorphous oxide semiconductor 'IGZO (Indium-Gallium-Zinc-Oxygen)' that we had developed, it was denied in South Korea for some reason. The reason for this rejection was that the invention was 'easy to analogize'. ~Omitted~ However, it is not easy to analogize from the conditions currently existing for amorphous silicon. I went to the Korean court as a witness and gave an evidence-based explanation of the history of semiconductors for about an hour in English. The judges understood my arguments and delivered a verdict in about a month. Normally, court cases like this would be entrusted to a law firm in the relevant country, but I was glad I went there and spoke to the court. A Korean company obtained the requisite license thereafter, but looking back, I think that if I had lost the case at that time, our patent might never have been put to use." (* There was a simple mistake in the original article, and "1 week" has been corrected to "1 month".)

While working at the university, Hosono published the IGZO-based oxide semiconductor thin-film transistor technology that he discovered and developed in an internationally renowned academic paper and also received dedicated support and cooperation from many members of the project and Canon, with whom he conducted joint research, and seems to have consulted several intellectuals with extensive experience in patent licensing and patent disputes. Armed with accurate advice and enthusiastic cooperation from such people, Hosono took the lead in responding to requests for invalidation trials and objections from SEL, which had been ongoing since around 2014, one by one, with great tenacity over 5 years until the final settlement in April 2019. He also traveled to other countries and conducted interviews with examiners and appeal examiners at the patent offices to help them understand the essence of the invention, resulting in the grant of many intellectual properties (rights), both in Japan and overseas. I can't help but be in awe of Hosono's extraordinary energy and efforts, such as bridging to the world's electronics manufacturers on materials technology.

Column: Trademark Registration of "IGZO"

It appears that Hosono and JST were not consulted prior to Sharp's trademark registration of "IGZO". More importantly, having received many concerns and inquiries from researchers through academic conferences and journals about whether the term "IGZO" can be published or mentioned in the future, JST filed a request for invalidation of the trademark registration of the substance name "IGZO" by Sharp (the application for trademark registration was submitted before the license agreement with JST) with the Japan Patent Office on July 31, 2013, and the invalidation was recognized by a trial decision of the Japan Patent Office the following year on March 5, 2014.

First, the term "IGZO" was already widely used and recognized as an abbreviation for raw materials in papers, international conferences and patents. The fundamental idea is that only one company, Sharp, cannot be granted exclusive use of the trademarked term "IGZO". In response to this reasonable ruling, Sharp appealed the decision to the Tokyo High Court's Intellectual Property High Court. However, on February 25, 2015, the Intellectual Property High Court ruled that Sharp's registered trademark was invalid because "the abbreviation IGZO is widely recognized as the name of a raw material". (Dismissal of claim by Sharp)

Sharp's allegation was, "JST is an organization that promotes science and technology and does not manufacture or sell products, and therefore lacks the eligibility requirements to be a petitioner for an invalidation trial." With this judgment, the Japan Patent Office, for the first time in the country's history, determined that even research and development organizations such as JST can become petitioners for invalidation trials against registration of trademarks, thus making this a landmark case[1), 2)]. This information was announced in the notification from JST mentioned above and also notified by Sharp at the same time[3)].

This trademark registration case has been covered from various angles and seems to serve as "educational material"[4)].

While writing this column, the authors recalled a truly bitter memory of publishing their IGZO research results in a

paper in which they stated that IGZO was a registered trademark of Sharp. Finally, I want to express my deepest respect to JST (Chairman: Michiharu Nakamura), which courageously took the initiative to request an invalidation trial despite its position as a national research and development organization.

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(Viewed on 07.01.2022)
＊Press release (Intermediate Message) dated April 24, 2014
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(Viewed on 07.01.2022)
2) Furthermore, during an interview with Dr. Masaru Ozaki (former Industry-Academia Partnership Advisor, Department of Intellectual Property Management, JST) on August 4, 2022, Dr. Ozaki handed me the information memo compiled by Mr. Masaharu Kubo, who belonged to the same team at the time. I summarized this column using this memo as one of the important references.
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28) K. M. Kojima, M. Hiraishi, H. Okabe, A. Koda, R. Kadono, K. Ide, S. Matsuishi, H. Kumomi, T. Kamiya and H. Hosono: "Electronic structure of interstitial hydrogen in In-Ga-Zn-O semiconductor simulated by muon", Appl. Phys. Lett., 115, 122104 (2019).
29) Based on the results of the author's interview with Dr. Masashi Furukawa (Manager, Department of Innovation Platform, JST / he belonged to the Special Project Promotion Department at the time.) on July 21 (Thursday), 2022.
30) Based on the results of the author's interview with Dr. Masaru Ozaki (former Industry-Academia Partnership Advisor, Department of Intellectual Property Management, JST) on August 4 (Thursday), 2022.
31) JST Signs Patent License Agreement with Samsung for High Performance Thin Film Transistor Technology, -Major Entry of Japanese Basic Research Results into Global Display Industry-: https://www.jst.go.jp/pr/anounce/20110720-2/index.html [in Japanese]
https://www.jst.go.jp/pr/announce/20110720-2/index_e.html [in English] (Viewed on 07.01.2022)
32) JST and Sharp sign license agreement on oxide semiconductors: https://www.jst.go.jp/report/2012/120529.html [in Japanese] (Viewed on 07.01.2022)
33) Sharp Begins Production of World's First LCD Panels Incorporating IGZO Oxide Semiconductors:
https://corporate.jp.sharp/report/igzo/index.html [in Japanese]
https://global.sharp/corporate/news/120413.html [in English] (Viewed on 07.01.2022)
34) Sharp and JST sign license agreement on oxide semiconductors: https://corporate.jp.sharp/news/120529-c.html [in Japanese] (Viewed on 07.01.2022)
35) Sharp and Semiconductor Energy Laboratory Jointly Develop New Oxide Semiconductor Technology That Will Revolutionize Displays:
https://corporate.jp.sharp/news/120601-a.html [in Japanese]
https://global.sharp/corporate/news/120601.html [in English] (Viewed on 07.01.2022)
https://corporate.jp.sharp/report/igzo2/index.html [in Japanese] (Viewed on 07.01.2022)
36) Professor Hideo Hosono receives "40th Harushige Inoue Award" for the development of the IGZO target
https://www.titech.ac.jp/news/2015/031856 [in Japanese]
https://www.titech.ac.jp/english/news/2015/031654 [in English] (Viewed on 08.05.2022)
https://www.titech.ac.jp/news/pdf/tokyotechpr20150716_

hosono.pdf [in Japanese]
(Viewed on 08.05.2022)

37) Toshio Kamiya, Hideya Kumomi and Hideo Hosono: "Amorphous Oxide Semiconductor Thin Films", J. Surf. Finish. Soc. Jpn., 64, <7>, 392-395 (2013). [in Japanese]

38) Yoshiyuki Matsuo: Interview Article with Professor Hideo Hosono, "Research Methods of Dr. Hideo Hosono" Journal of Industry-Academia-Government Collaboration, Vol.9, No.9, 4-21 (2013).
https://www.jst.go.jp/tt/journal/journal_contents/before2015/pdf/2013/1309-all.pdf [in Japanese] (Viewed on 08.06.2022)

39) Information on the 12th Nikkei BP's Japan Innovators Award:
- Professor Hideo Hosono Honored with the Excellence Award of Nikkei BP's Japan Innovators Award 2013;
https://www.titech.ac.jp/news/2013/023776 [in Japanese]
https://www.titech.ac.jp/english/news/2013/023791 [in English]
(Viewed on 08.06.2022)
- Professor Hideo Hosono Honored with the Excellence Award of Nikkei BP's Japan Innovators Award 2013;
https://www.jst.go.jp/report/2013/131025.html [in Japanese]
https://www.jst.go.jp/report/2013/131119_3_e.html [in English]
(Viewed on 08.06.2022)

40) Information on the 2nd Intellectual Property Special Contribution Award:
- Intellectual Property Special Contribution Award to Dr. Hideo Hosono:
https://scienceportal.jst.go.jp/newsflash/20150225_05/index.html [in Japanese]
(Viewed on 08.06.2022)
- Details of the 2nd Intellectual Property Special Contribution Award:
https://www.jst.go.jp/pr/info/info1083/besshi.html [in Japanese]
(Viewed on 08.06.2022)
- Professor Hideo Hosono receives the 2nd Intellectual Property Special Contribution Award:
https://www.titech.ac.jp/news/2015/030103 [in Japanese]
https://www.titech.ac.jp/english/news/2015/030215 [in English]
(Viewed on 08.06.2022)
- A group photo of the people involved in the award is available at the JST URL in reference (44) below: (Viewed on 07.01.2022)
https://www.jst.go.jp/tt/journal/journal_contents/2019/11/1911-02_article.html [in Japanese]

41) Japan Science and Technology Agency (JST): "To whom interested in Research & Development and/or Business Development of "IGZO-based Oxide Semiconductor TFT"":
- Press release (Final Message) dated July 17, 2019:
https://www.jst.go.jp/chizai/IGZO.html [in Japanese]
(Viewed on 07.01.2022)
- Press release (Intermediate Message) dated April 24, 2014
https://www.jst.go.jp/osirase/20130515_e.html [in English]
(Viewed on 07.01.2022)

42) [Notice from JST] Initiatives to Protect and Utilize Intellectual Property Rights Related to Research Results:
https://www.jst.go.jp/chizai/docs/20190611.pdf [in Japanese]
(Viewed on 07.01.2022)

43) JST: IGZO Patent Lawsuit Settled; Professor Hideo Hosono's Invention Approved:
https://www.keguanjp.com/kgjp_jingji/imgs/2019/06/20190620_1.pdf [in Japanese]
(Viewed on 07.01.2022)

44) Yasuhiro Yamaguchi: "Close-up: Materials are useful when they contribute to society", Journal of Industry-Academia-Government Collaboration, (November 2019).
https://www.jst.go.jp/tt/journal/journal_contents/2019/11/1911-02_article.html [in Japanese]
(Viewed on 07.01.2022)
Or you can also check the following websites.
https://www.jstage.jst.go.jp/article/sangakukanjournal/15/11/15_4/_pdf [in Japanese]

45) Communication with Professor Hideo Hosono (December 31, 2022)

46) researchmap: "file_03: In Korean Courts,"
https://article.researchmap.jp/column/201111_3/ [in Japanese]
(Viewed on 08.05.2022)

7 Subsequent R&D Trends and Technological Developments and Spillovers in IGZO-Related Materials and Devices

7.1 Dramatical Change of The Fields of Expertise of Journals to which Papers are Submitted and Conferences in which Research Results are Presented —from Materials Research to Semiconductor Electronics Development—

To understand the overview of the IGZO-related papers published by researchers and presentations at international conferences around the world since the publication of Hosono's paper in *Nature*, I used my methods to survey how papers and presentations at international conferences have evolved from the perspective of materials and physical properties to a wide range of electronics applications, such as display applications, semiconductor circuits, memory, and sensors. For details on the survey method, please refer to the end of the chapter.

The results obtained from the four surveys [(i), (ii), (iii), and (iv)] are shown in Fig. 7.1 to Fig. 7.4 as bar charts with the years 2005 through 2022 along the horizontal axis and the number of papers or international conference presentations along the vertical axis.

The following situations can be inferred from the results.

○ Around 2010, overcoming stability issues was the remaining challenge. However, as these challenges were addressed, the number of papers peaked around 2013 and has been steadily decreasing since then, suggesting that research on IGZO-based materials is approaching its conclusion.

○ From the trends in high-impact international materials science journals, it can be inferred that a new research direction focusing on high-performance materials and devices has emerged. In particular, *Advanced Electronic Materials* published nearly 30 articles related to IGZO technologies in 2015, and future developments are expected.

○ The number of research presentations in the display field is steadily increasing, which may prove that "IGZO-TFT" technology remains attractive. Since 2018, the count has plateaued, with approximately 30 papers being published each year, suggesting that there might be advancements towards mass production. Indeed, display products from numerous companies are making their way into the market.

○ Even in the semiconductor electronics field, there has also been a steady increase in publications. Since 2007, "a-IGZO TFT" technology has been progressively making its mark in the semiconductor electronics sector, including applications in memory and sensors, by incorporating new types of oxide transistors.

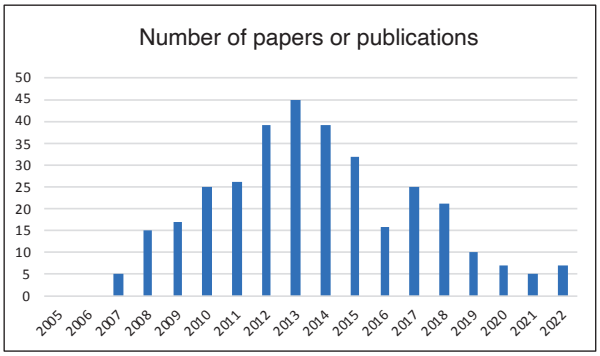

Fig. 7.1 Case (i): Number of IGZO-related papers published in *Appl. Phys. Lett.* and *J. Appl. Phys.* et al. by year.

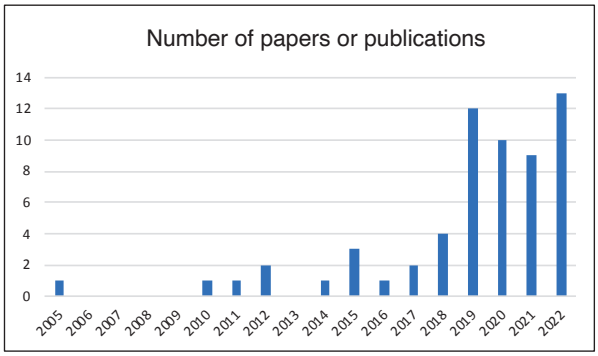

Fig. 7.2 Case (ii): Number of IGZO-related papers published in *Advanced Materials* and its sister journals by year.

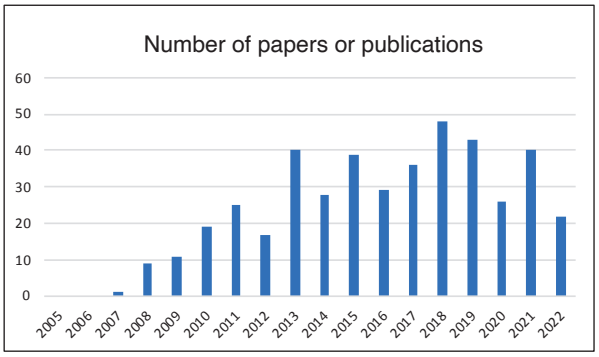

Fig. 7.3 Case (iii): Number of IGZO-related papers presented at prominent international conferences in the display field, such as *SID* International Conference by year.

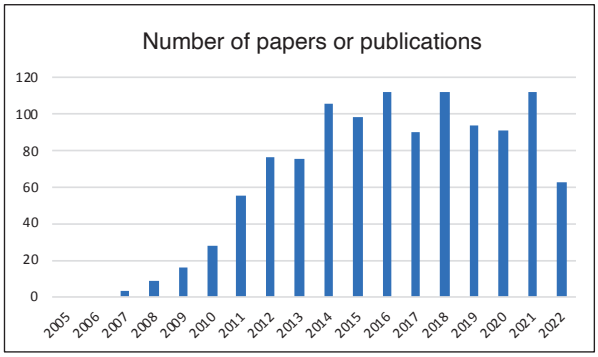

Fig. 7.4 Case (iv): Number of IGZO-related papers presented at prominent international conferences in the *IEEE* semiconductor electronics field by year.

Column: Hosono Group's Presentations have Expanded beyond International Conferences on Materials to Them Focused on Semiconductor Electronics

The core focus of Hideo Hosono as a researcher is on "material creation". However, I would like to mention in this column that following the publication in *Nature* in 2004, the group led by Hideo Hosono has devoted significant effort to the penetration and widespread adoption of "a-IGZO TFT" among researchers and developers in the field of semiconductor electronics worldwide.

The list of presentation titles by the Hosono Group at SID (The Society for Information Display) conferences, specialized journals on electronics, and semiconductor-related international conferences since 2007 are shown in Table 7.1. Especially in the display field, the Hosono Group has presented as many as 34 papers related to IGZO research at major events such as the SID Display Week International Symposium and the AM-FPD Workshop, which rank among the largest conferences in the world for display technologies. As a university researcher, Hosono traditionally focused on materials, physics, and chemistry and has shown significant expansion beyond his usual scope of activities. Indeed, Hideo Hosono's unwavering conviction in the potential of the "a-IGZO TFT technology" as a "practical material technology" is undeniable proof of his role as a bridge to industrialization, personally undertaken by him.

Table 7.1 A list of presentations by the Hosono Group at SID and IEEE related international conferences for each year

Year	Titles	Papers/International Conferences
2007	68.3: Invited Paper: Transparent Amorphous Oxide Semiconductors for High Performance TFT	SID Symposium Digest of Technical Papers, 38, Issue 1
	Circuits using uniform TFTs based on amorphous In-Ga-Zn-O	Journal of the Society for Information Display, 15, Issue 11
	Fast Thin-Film Transistor Circuits Based on Amorphous Oxide Semiconductor	IEEE Electron Device Letters, 28, Issue 4
2008	P-29: Modeling of Amorphous Oxide Semiconductor Thin Film Transistors and Subgap Density of States	SID Symposium Digest of Technical Papers, 39, Issue 1
	P-13: Photosensitivity of Amorphous IGZO TFTs for Active-Matrix Flat-Panel Displays	SID Symposium Digest of Technical Papers, 39, Issue 1
	42.1: Invited Paper: Improved Amorphous In-Ga-Zn-O TFTs	SID Symposium Digest of Technical Papers, 39, Issue 1
2009	Origins of High Mobility and Low Operation Voltage of Amorphous Oxide TFTs: Electronic Structure, Electron Transport, Defects and Doping	Journal of Display Technology, 5, Issue 7
	Origins of High Mobility and Low Operation Voltage of Amorphous Oxide TFTs: Electronic Structure, Electron Transport, Defects and Doping*	Journal of Display Technology, 5, Issue 12
	Electronic Structures Above Mobility Edges in Crystalline and Amorphous In-Ga-Zn-O: Percolation Conduction Examined by Analytical Model	Journal of Display Technology, 5, Issue 12
2010	Interface and bulk effects for bias-light-illumination instability in amorphous-In-Ga-Zn-O thin-film transistors	Journal of the Society for Information Display, 18, Issue 10
2011	Diffusion-Limited a-IGZO/Pt Schottky Junction Fabricated at 200°C on a Flexible Substrate	IEEE Electron Device Letters, 32, Issue 12
	Simple Analytical Model of On Operation of Amorphous In-Ga-Zn-O Thin-Film Transistors	IEEE Transactions on Electron Devices, 58, Issue 10
	35.5L: Late-News Paper: An Ambipolar Oxide TFT	SID Symposium Digest of Technical Papers, 42, Issue 1
2012	Amorphous In-Ga-Zn-O Dual-Gate TFTs: Current-Voltage Characteristics and Electrical Stress Instabilities	IEEE Transactions on Electron Devices, 59, Issue 7
	Characteristic shift of a CTFT inverter using n-type IGZO and p-type F8T2 TFTs after temperature and operation stresses	IEEE International Meeting for Future of Electron Devices
	Light Irradiation History Sensor Using Amorphous In-Ga-Zn-O Thin-Film Transistor Exposed to Ozone Annealing	IEEE Electron Device Letters, 33, Issue 3
2013	4.1: Invited Paper: Electronic Structure, Carrier Transport, Defects and Impurities in Amorphous Oxide Semiconductor	SID Symposium Digest of Technical Papers, 44, Issue 1
	P.3: 3-D Stacked Complementary TFT Devices using n-type α-IGZO and p-type F8T2 TFTs – Operation Confirmation of NOT and NAND Logic Circuits –	SID Symposium Digest of Technical Papers, 44, Issue 1
	P.142L: Late-News Poster: Electron Injecting Material for OLEDs driven by Oxide TFTs: Amorphous C12A7 Electride	SID Symposium Digest of Technical Papers, 44, Issue 1
	Light irradiation history sensor using amorphous In-Ga-Zn-O thin-film transistor fabricated by high oxygen partial pressure sputtering	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Current status and future challenge of oxide semiconductors	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
2014	Positive Gate Bias Instability Induced by Diffusion of Neutral Hydrogen in Amorphous In-Ga-Zn-O Thin-Film Transistor	IEEE Electron Device Letters, 35, Issue 8
	Positive-Bias Stress Test on Amorphous In-Ga-Zn-O Thin Film Transistor: Annealing-Temperature Dependence	Journal of Display Technology, 10, Issue 11
	Effects of High-Temperature Annealing on Operation Characteristics of a-In-Ga-Zn-O TFTs	Journal of Display Technology, 10, Issue 11
	Light irradiation and applied voltage history sensors using amorphous In-Ga-Zn-O thin-film transistors exposed to ozone annealing and fabricated under high oxygen pressure	21st International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)

2015	P-177L: Late-News Poster: Highly Efficient Inverted OLEDs using A New Transparent Amorphous Oxide Semiconductor	SID Symposium Digest of Technical Papers, 46, Issue 1
	P-176L: Late-News Poster: Deposition and Structuring Processes of a Newly Developed Transparent Amorphous Oxide Semiconductor for the Electron Transport and Injection Layers of AM-OLEDs	SID Symposium Digest of Technical Papers, 46, Issue 1
	Origin of Lower Film Density and Larger Defect Density in Amorphous In-Ga-Zn-O Deposited at High Total Pressure	Journal of Display Technology, 11, Issue 6
	Charge Compensation by Excess Oxygen in Amorphous In-Ga-Zn-O Films Deposited by Pulsed Laser Deposition	Journal of Display Technology, 11, Issue 6
2016	31-4: Novel Inorganic Electron Injection and Transport Materials Enabling Large-Sized Inverted OLEDs Driven by Oxide TFTs	SID Symposium Digest of Technical Papers, 47, Issue 1
	69-4: NBIS-Stable Oxide Thin-Film Transistors Using Ultra-Wide Bandgap Amorphous Oxide Semiconductors	SID Symposium Digest of Technical Papers, 47, Issue 1
	Novel oxide semiconductors for OLEDs and catalysis	2016 Compound Semiconductor Week (CSW) [Includes 28th International Conference on Indium Phosphide & Related Materials (IPRM) & 43rd International Symposium on Compound Semiconductors (ISCS)
	Why high-pressure sputtering must be avoided to deposit a-In-Ga-Zn-O films	23rd International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
2017	P-13: Quantitative Analysis and Deconvolution of Subgap States in Amorphous In-Ga-Zn-O	SID Symposium Digest of Technical Papers, 48, Issue 1
	P-234: Late-News Poster: OLED Lighting with High Out-Coupling Efficiency and Reliability	SID Symposium Digest of Technical Papers, 48, Issue 1
	P-187: Electronic Structures of Various Color Light-Emitting Amorphous Oxide Semiconductor Thin Films	SID Symposium Digest of Technical Papers, 48, Issue 1
	Transparent amorphous oxide semiconductors: Materials design, electronic structure, and device applications	75th Annual Device Research Conference (DRC)
	Material design of ultra-wide bandgap AOSs and their applications in photostable electronic devices	24th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
2018	19-4: Late-News Paper: New P-type Amorphous Semiconductor with High Transparency and High Mobility of 9 cm^2/Vs for Next-Generation Displays	SID Symposium Digest of Technical Papers, 49, Issue 1
	Solution-Processable P-type Transparent Amorphous Semiconductor for Flexible Electronics	25th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
2019	P-197: Late-News Poster: NBTS-free Oxide TFTs with High Mobility of 40 cm^2/Vs: A Possible Origin for NBTS Instability	SID Symposium Digest of Technical Papers, 50, Issue 1
	New Amorphous In-Ga-Zn-O Thin-Film Transistor-Based Optical Pixel Sensor for Optical Input Signal With Short Wavelength	IEEE Transactions on Electron Devices, 66, Issue 9
2020	Electronic defects in amorphous oxide semiconductor and recent development	27th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
2021	15.1: Invited Paper: Understanding and controlling electronic defects in amorphous oxide semiconductor	SID Symposium Digest of Technical Papers, 52, Issue S1
	Unintended Carbon-Related Impurity and Negative Bias Instability in High-Mobility Oxide TFTs	IEEE Electron Device Letters, 42, Issue 9

The photo shown in Fig. 7.5 is from 2017, when the former president (current advisor) of LG Display, Sang-deog Yeo, donated the latest OLED TV to the research center where Hosono is affiliated and delivered a public lecture.

Fig. 7.5 Commemorative photograph of then President Sang-deog Yeo (left) and Professor Hideo Hosono (right) with the donated LG Display OLED-TV in the background. (This Photograph is courtesy of Prof. Hideo Hosono.)
The hall was packed for the public lecture held on that day. This is a valuable photograph that proves a concrete example of bridging the gap between academia and industry with Professor Hosono's materials technology.

From the above observations, it can be inferred that today, the presentation of oxide semiconductor transistors has significantly shifted from the stage of fundamental research on material properties to the stage of semiconductor electronics with a focus on practical applications. The "a-IGZO TFT" technology, discovered and invented by Hideo Hosono, can be said to have steadily taken off from the field of materials research and begun to soar into the vast expanse of semiconductor electronics.

I want to share another important survey data here. The survey results of investigating the citation trends for the papers published in *Science* in 2003 and *Nature* in 2004 for each respective year are shown in Fig. 7.6. Scopus was the survey tool used, and the survey date was October 5, 2022. At the time of the investigation, the number of citations for *Nature* was 6198, while for *Science*, it was 1713.

The citation count for both papers is very high. In particular, the citation count for the *Nature* paper, which reported on amorphous IGZO-TFT, is extremely high, reflecting its high potential for practical application. Furthermore, the citation count has grown substantially and significantly each year since the papers were published. The citation count of *Nature* paper peaked in 2015 and has been gradually decreasing in recent years, even today, 18 years after publication, maintaining nearly 300 citations in a single year is remarkable. The audience referencing Hideo Hosono's papers is presumed to have shifted from basic materials researchers at universities to researchers in the semiconductor electronics field and development researchers at private companies. Furthermore, the papers in *Science* reporting on transistors using oxide crystals have also seen a gradual decrease in citation counts from around 2012. However, a certain number has been maintained. Indeed, a reasonable assumption is that a certain number of researchers are interested in the development of crystalline IGZO-TFTs, as evidenced by their references to transistors using crystals.

The annual trends of the long-term citation counts for the 2 papers in *Nature* and *Science* journals vividly demonstrate that the research results have achieved significant technological dissemination. This evidence indicates that the seeds of technology are steadily penetrating and beginning to take root in society.

7.2 Application of "Oxide-TFT" to Displays and Its Development Status

Although it was mentioned that the invention of "a-IGZO TFT" technology could provide an alternative to "a-Si TFT" used in conventional flat-panel displays, this image seems to have been reinforced after the international conference, "International Workshop on Transparent Amorphous Oxide Semiconductors (TAOS 201)" on transparent amorphous oxide semiconductors (TAOS) and their application in displays, held on January 25, 2010, led by Hosono et al. of Tokyo Tech.

On the first day of the conference, following an opening talk by Hosono, the proceedings commenced with a keynote speech[1)] by Jun H. Souk, the former Vice President and then Senior Advisor at Samsung Electronics in South Korea. He asked the question, "Why do we need "High Mobility TFTs"?" and the slide that he showed in response to this ques-

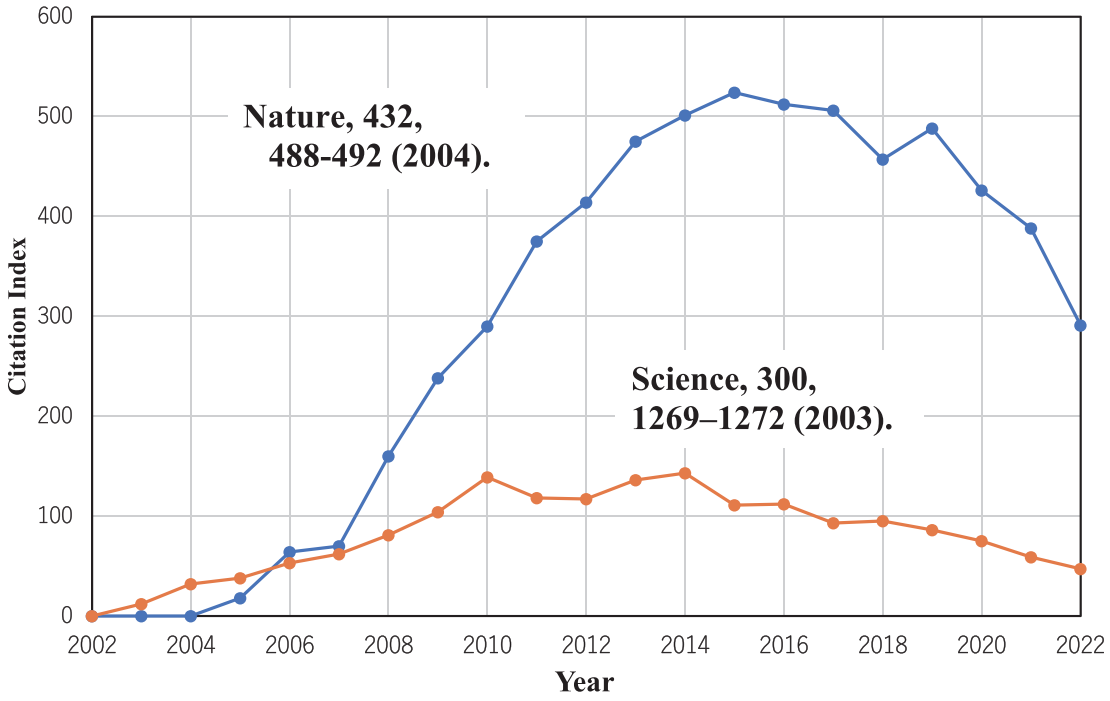

Fig. 7.6 Change from year to year of citation counts for Hosono's *Nature* and *Science* papers.
[Survey tool: Scopus; Survey date: October 5, 2022.]

tion illustrated the relationship between display resolution and refresh rate, as shown in Fig. 7.7. The main focus was on the need of high mobility TFTs for larger display areas and higher resolution. The recommendation was the early commercialization of a-IGZO TFT, a promising candidate. The author also participated in this TAOS conference and recalls that there was so much enthusiasm at the venue overflowing with participants, reminding him of the "high-temperature superconductivity fever" around 1987-1988.

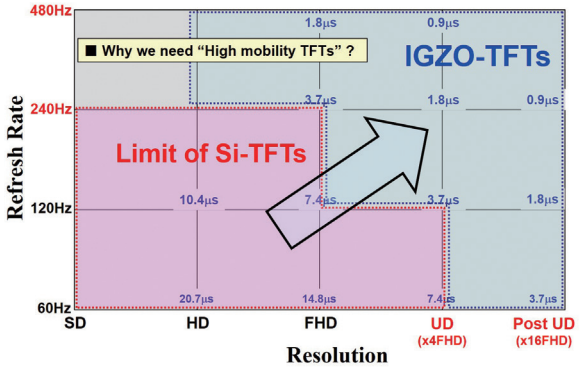

Fig. 7.7 Relationship between resolution and refresh rate in display.
(Based on slides presented by Dr. Jun H. Souk[1], redrawn by the author.)

At an international conference held in Himeji on January 28-29, 2010, technical consultant Yojiro Matsueda delivered a speech on the performance requirements of TFTs for next-generation flat-panel display (FPD) substrates, in which he mentioned the need for high-mobility TFTs, with displays becoming larger in area (increase in the number of pixels)[2]. Technical consultant Yasuhiro Ukai also sensed the transition from amorphous silicon to oxide transistors, he published a paper in the Journal of *the Japan Society of Applied Physics* discussing the history of thin film transistors and their prospects for the future[3]. Looking back today, after around 2010, the "a-IGZO TFT" technology began to permeate not only among academic researchers but also in the industrial world, leading to significant innovation; it seemed to be a period of great vitality worldwide. Fig. 7.8 shows a map of research institutions worldwide conducting oxide transistor-related research until about 2010, meticulously organized by Hideya Kumomi, a specially appointed professor at Tokyo Tech.

Kamiya of Hosono's Group published papers on transparent amorphous oxide semiconductors from the physical images of the materials to the application development, including some product images as of 2010[4, 5]. Furthermore, a collaborative research team from Hanyang University and KAIST in South Korea has also published a review paper[6], including images of products using oxide semiconductor transistors, as

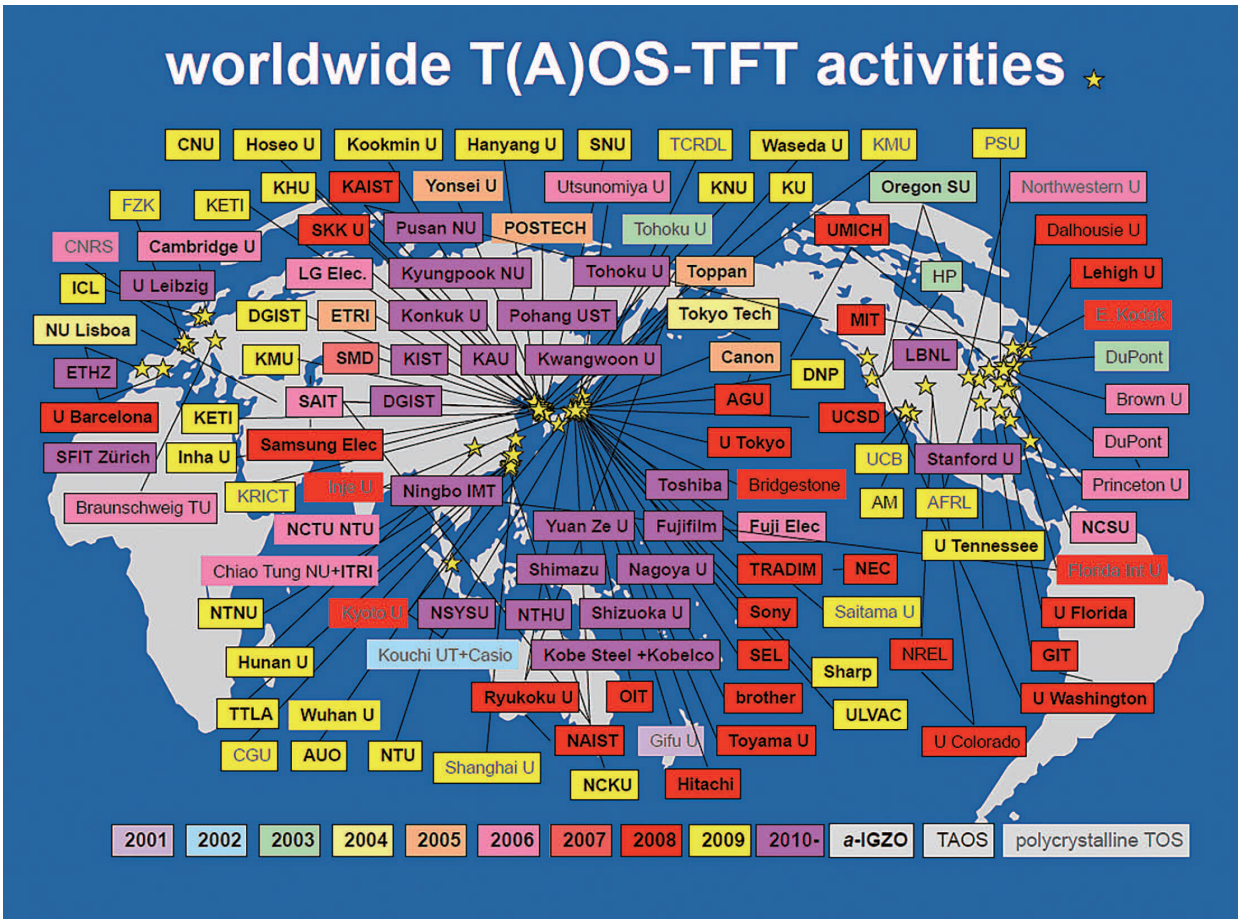

Fig. 7.8 Map of research activities related to oxide transistor worldwide. [until about 2010]
(This illustration is courtesy of Dr. Hideya Kumomi, Specially-Appointed Professor at Tokyo Institute of Technology.)

of 2014. In addition, in July 2018, Hosono published a column focused on "Development History of a-IGZO TFT" in the *Nature Electronics* journal[7]. This column is the so-called "IGZO development story", also covered in a news release by Tokyo Tech[8]. Fig. 7.9 shows the images of products considered to be equipped with oxide TFTs.

During the market development of "IGZO-TFT", precise information such as which company's products are equipped with oxide transistors is often veiled in secrecy and doesn't go beyond hearsay. One reason may be that only Sharp and Samsung Electronics in South Korea have publicly disclosed the conclusion of licensing agreements for Hosono et al.'s basic patents. Given that many companies are still in the midst of competition to develop products, they may need to keep such details confidential for business strategy reasons. However, there is no denying that many companies are benefiting from the "IGZO-TFT" technology.

At the 2014 SID International Conference, Matsuo et al. of Sharp presented a forecast showing a significant transition from a-Si TFT in the past to IGZO-TFT in the future[9]. Furthermore, J. F. Wager, a professor of Oregon State University in the U.S., has provided a detailed list of displays equipped with oxide-based TFTs, which are believed to be marketed as products, in his paper[10]. The contents of the list are summarized in Table 7.2. However, since not all display manufacturers have officially announced that their products are equipped with oxide TFTs, it is difficult for the public to know the actual situation.

On the other hand, Sharp, which has officially entered into patent licensing agreements with JST, began disclosing the development details of In-Ga-Zn-O thin film transistors, particularly around 2012, through academic journals, etc., which seemed to be a strategic move[11)-19)]. Especially the description in the literature[13] contains the history of IGZO and the strategy for its full-scale introduction, along with the background of Hosono's involvement in the JST project, serving as a resource[13], from which Sharp's future development strategy can be easily understood. The following is an excerpt of the important passages.

> "**The History of IGZO:** 'IGZO' is an oxide of indium (In), gallium (Ga), and zinc (Zn), and is a type of material commonly referred to as an 'oxide semiconductor'. The fundamental technology behind 'IGZO' was invented by Professor Hosono and his group at the Tokyo Institute of Technology as part of JST's Creative Science and Technology Promotion Project, for which several patents

Fig. 7.9 Image of a group of products thought to be equipped with oxide semiconductor transistors.
(These illustration and photographs are courtesy of Prof. Hideo Hosono.)

Table 7.2 A list of products thought to be equipped with oxide (IGZO-based)-TFTs

(Prof. John F. Wager of Oregon State University quickly surveyed products on the market as of mid-October 2015 and published in Information Display (2016)[10] promptly. The author rearranged the order of the products in the table in his paper (10), as shown here. Note that there is no assurance that individual products are always equipped with oxide TFTs, but on the other hand, it is estimated that more and more products are now using oxide

Maker	Products (Display)
< TV >	
LG Display	Smart OLED TV 55EG9100 54.6", 1920 × 1080, 40 ppi
LG Display	Smart 3D OLED TV 55EF9500 54.6", 3840 × 2160, 81 ppi
LG Display	Smart 3D OLED TV 65EF9500 64.5", 3840 × 2160, 68 ppi
LG Display	Smart 3D Curved OLED TV 55EC9300 54.6", 1920 × 1080, 40 ppi
LG Display	Smart 3D Curved OLED TV 55EG9600 54.6", 3840 × 2160, 81 ppi
LG Display	Smart 3D Curved OLED TV 65EG9600 64.5", 3840 × 2160, 68 ppi
LG Display	Smart 3D Curved OLED TV 65EG9700 64.5", 3840 × 2160, 68 ppi
LG Display	Smart 3D Curved OLED TV 77EG9700 76.7", 3840 × 2160, 57 ppi
Sharp	LV-85001 85", 7680 × 4320, 104 ppi
< Phone >	
Sharp	Aquos Compact SH-02 4.7", 1080 × 1920, 469 ppi
Sharp	Aquos Xx2 mini 4.7", 1080 × 1920, 469 ppi
Sharp	Aquos Xx2 (502SH) 5.3", 1080 × 1920, 415 ppi
Sharp	Aquos Zeta SH-01 5.5", 1080 × 1920, 401 ppi
Sharp	Aquos Zeta SH-02 4.7", 720 × 1280, 300 ppi
Sharp	Aquos Zeta SH-03 5.5", 1080 × 1920, 401 ppi
Sharp	Aquos Zeta SH-04 5.4", 1080 × 1920, 408 ppi
Sharp	Aquos Zeta SH-06 4.8", 1080 × 1920, 459 ppi
Kyocera	m1 note 5.5", 1080 × 1920, 401 ppi
Meizu	m2 note 5.5", 1080 × 1920, 401 ppi
Meizu	MX5 5.5", 1080 × 1920, 401 ppi
Meizu	Infobar A03 4.5", 1080 × 1920, 490 ppi
ZTE	Torque G02 4.7", 720 × 1280, 312 ppi
ZTE	Nubia Z5S 5", 1080 × 1920, 441 ppi
Xiaomi	Nubia Z5S mini 4.7", 720 × 1280, 312 ppi
Kyocera	Readmi 2 Prime 4.7", 720 × 1280, 312 ppi
< Desktop >	
Apple	iMac with 5K Retina display 27", 5120 × 2880, 218 ppi
Apple	21.5" iMac with 5K Retina display 21.5", 4096 × 2304, 218 ppi

Maker	Products (Display)
< Monitor >	
Sharp	LQ-101R1SX03 10.1", 2560 × 1600, 299 ppi
Sharp	PN-K322B 31.5", 3840 × 2160, 140 ppi
Sharp	PN-321Q 31.5", 3840 × 2160, 140 ppi
Dell	UltraSharp UP3214Q 31.5", 3840 × 2160, 140 ppi
Dell	UltraSharp UP3216Q 31.5", 3840 × 2160, 140 ppi
NEC	PA322UHD-BK-SV 31.5", 3840 × 2160, 140 ppi
< Tablet >	
Cube	i6 Air 9.7", 2048 × 1536, 264 ppi
Apple	iPad Pro 12.9", 2732 × 2048, 264 ppi
Lenovo	LaVie Z 13.3", 2560 × 1440, 221 ppi
Fujitsu	Lifebook S935 13.3", 1920 × 1280, 221 ppi
Fujitsu	Lifebook T935 13.3", 2560 × 1440, 221 ppi
Fujitsu	Lifebook T904 13.3", 2560 × 1440, 221 ppi
Fujitsu	Lifebook U904 14", 4300 × 1800, 262 ppi
Teclast	P98 Air 9.7", 2048 × 1536, 264 ppi
Onda	V919 Air 9.7", 2048 × 1536, 264 ppi
< Laptop >	
Toshiba	Radius 12 12.5", 3840 × 2160, 352 ppi
Toshiba	Satellite P55t-B5262 15.6", 3840 × 2160, 282 ppi
NEC	Skylake NS850 15.6", 3840 × 2160, 282 ppi
NEC	VersaPro Type VG 13.3", 2560 × 1440, 221 ppi
Dell	XPS 12 (option) 12.5", 1920 × 1080, 176 ppi
Dell	XPS 15 (option) 15.6", 3840 × 2160, 282 ppi
< Gaming Laptop >	
Alienware	Alienware 13 (option) 13.3", 3200 × 1800, 276 ppi
Alienware	Alienware 17 (option) 17.3", 3840 × 2160, 255 ppi
Razor	Razor 14" Blade 14", 3200 × 1800, 262 ppi
Aorus	X3 Plux v3 13.3", 3200 × 1800, 276 ppi
Aorus	X3 Plus v4 13.9", 3200 × 1800, 264 ppi

have been obtained. In 2004, Professor Hosono and his group used this technology to prototype TFTs (thin film transistors). They discovered that electron mobility, an indicator of the ease with which electrons flow through the device, was an order of magnitude higher than TFTs using amorphous silicon, the material used in conventional LCD panels. This achievement was published in scientific journal '*Nature*' in November 2004.

A New Trend in Semiconductor Technology: Sharp, in collaboration with Semiconductor Energy Laboratory Co., Ltd., developed TFTs using 'IGZO' and successfully mass-produced the world's first LCD panels using "IGZO". 'IGZO' will bring innovative change to electronic devices using semiconductors, such as LSIs and LCDs. This is because its basic characteristics are significantly superior to silicon (Si), which has been the mainstream semiconductor material until now. Specifically, when deployed in a transistor, which is a switching device, the mobility of electrons flowing through the device in the ON state is high. Moreover, the leakage current flowing in the OFF state is small. It was impossible to achieve both basic characteristics in conventional transistors using silicon. In other words, 'IGZO' can be considered a groundbreaking semiconductor technology that overturns conventional wisdom. There is a possibility that 'IGZO' will replace silicon, which has been used since the invention of ICs (integrated circuits). In that case, 'IGZO' would have an immeasurable impact on people."

On April 24, 2019, Sharp announced the development of the "5th generation IGZO (IGZO5)" LCD panel with low power consumption, which will be used in future large-screen 80-inch 8K LCDs, mobile devices, displays and professional monitors, and also a wide range of applications will be developed for medium-sized OLED displays[20]. Additionally, top-gate type IGZO TFTs were developed for the backplane of OLED displays for automotives[21].

In a recent paper[22] by CEO of Hendy Consulting Limited Ian Hendy et al., the "IGZO-TFT" technology created by Hosono is evaluated as a pioneer of new semiconductor options that can be alternatives to a-Si or LTPS in LCDs requiring higher frame rates and in OLED displays. The paper also introduces in detail specific efforts by various companies for various displays and IT tools from a global perspective. Further information, including various data, can be found in the Appendix[23]. Similarly, from a future perspective, the paper reports evaluations for four types of transistor materials: LTPS (Low Temperature Poly Silicon), a-Si, oxides such as IGZO, and organic semiconductors, based on six categories: Mobility, Printability, Flexibility, CMOS Capability, Spatial Uniformity, and Transparency, and it is expected that new wearable, flexible, and transparent electronic devices will increase[24].

Sharp and R&D institutions worldwide are expected to develop various applications in the future.

7.3 Notable Research Results and Technological Spillovers on the Application of IGZO-Related Materials

7.3.1 Developments of CAAC-IGZO Technology

Semiconductor Energy Laboratory Co., Ltd. (Hereafter briefly abbreviated as SEL) is well known for its amorphous silicon technology and flat panel semiconductor technology and is particularly well known for its high activity in intellectual property. Shunpei Yamazaki, the president of the company, has a profile of being the No.1 patent holder in the Guinness Book of World Records[25].

Since the announcement of amorphous IGZO-based oxide semiconductor TFTs in Nature by Hideo Hosono et al. in November 2004, SEL has been catching up with "Hosono's IGZO technology and information" at an early stage and has combined the display-related technologies and device technologies cultivated in-house over the years. The company is developing with an eye toward practical application at an extremely rapid pace.

SEL is noteworthy for its unusually large number of technical publications and international conferences, including its own material technology. In some cases, especially presentations at prominent international conferences are joint research with Sharp. SEL and Sharp have a history of joint development of the world's first Continuous Grain Silicon (also called CG silicon) technology in 1998[26), 27)]. Given the history of these two companies, it is thought that the organization of SEL and Sharp's collaboration is certainly playing a role in the industrialization of "IGZO-TFT."

Examples of academic publications that provide evidence for this include *the Japanese Journal of Applied Physics (JJAP)*[28)-52)] of the Japan Society of Applied Physics, ECS-related journals[53)-71)] of Electrochemical Society Inc., and AIP-related journals[72)-74)] of American Institute of Physics. In addition, there are many papers related to SEL's proprietary material and device technology, such as papers presented at the SPIE conference[75)] and *International Journals of Ceramics Engineering*[76)]".

To add to this, the focus of SEL's activities seems to be on international conferences related to displays or semiconductor electronics, presumably as part of its corporate strategy. Table 7.3 summarizes a number of IGZO-TFT-related announcements by SEL extracted from the search for SID-related and IEEE-Xplore-related activities. As can be seen from this table, SEL has more than 80 presentations at the world's largest international SID display conferences (including J. SID journal) since 2009, and SEL has also presented on oxide semiconductor device and process technologies at the IEEE International Electron Devices Meeting (IEDM) and the International Solid -State Circuits Conference (ISSCC), the two major international conferences in the semiconductor field. From these facts, it is judged that SEL is developing at a very high activity level internationally. SEL, in particular, has several joint announcements with Sharp, related to display technology. It is very likely that Sharp, a large global company that has a driving force in the industry, could have moved the entire flat panel display industry by publicly announcing a piece of display technology used oxide semiconductor transistors.

Table 7.3 A list of presentations by Semiconductor Energy Laboratory Co., Ltd. (SEL) at SID and IEEE related international conferences for each year.

Year	Titles	Papers/International Conferences
2009	15.2: Development of Driver-Integrated Panel Using Amorphous In-Ga-Zn-Oxide TFT	SID Symposium Digest of Technical Papers, Volume 40, Issue 1
	P-9: Numerical Analysis on Temperature Dependence of Characteristics of Amorphous In-Ga-Zn-Oxide TFT	SID Symposium Digest of Technical Papers, Volume 40, Issue 1
	21.3: 4.0 In. QVGA AMOLED Display Using In-Ga-Zn-Oxide TFTs with a Novel Passivation Layer	SID Symposium Digest of Technical Papers, Volume 40, Issue 1
2010	18.3: Low Power 3.4inch Quarter High Definition OLED Display Using InGaZnOxide TFTs and White Tandem OLED	SID Symposium Digest of Technical Papers, Volume 41, Issue 1
	76.1: High Aperture Ratio LCD Display using In-Ga-Zn-Oxide TFTs without Storage Capacitor	SID Symposium Digest of Technical Papers, Volume 41, Issue 1
	43.4: Low Power LC Display Using In-Ga-Zn-Oxide TFTs Based on Variable Frame Frequency	SID Symposium Digest of Technical Papers, Volume 41, Issue 1
	P-143: Possibility of Reflective LC Display Using Oxide Semiconductor TFTs as Electronic Paper Display	SID Symposium Digest of Technical Papers, Volume 41, Issue 1
	7.3: Development of 3.4in. QHD LCD Having Blue Phase LC and Oxide Semiconductor TFTs	SID Symposium Digest of Technical Papers, Volume 41, Issue 1
	Driver-circuits-integrated LCDs based on novel amorphous In-Ga-Zn-oxide TFT	Journal of the Society for Information Display, Volume 18, Issue 4
2011	C-Axis Aligned Crystalline In-Ga-Zn-Oxide FET with High Reliability	18th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	50.2: High Reliable In-Ga-Zn-Oxide FET Based Electronic Global Shutter Sensors for In-Cell Optical Touch Screens and Image Sensors	SID Symposium Digest of Technical Papers, Volume 42, Issue 1
	28.2: Color Sequential LC Display Using High Reliable Oxide Semiconductors with Monochrome Electronic Paper Function	SID Symposium Digest of Technical Papers, Volume 42, Issue 1
	49.4: High-definition Top-emitting AMOLED Display with Highly Reliable Oxide Semiconductor Field Effect Transistors	SID Symposium Digest of Technical Papers, Volume 42, Issue 1
	36.4: 3.4-inch Full-Color QHD AMOLED Display using Large-Size Flexible Substrate with Highly Reliable OS-FETs	SID Symposium Digest of Technical Papers, Volume 42, Issue 1

Year	Titles	Papers/International Conferences
2011	Electronic global shutter CMOS image sensor using oxide semiconductor FET with extremely low off-state current	Symposium on VLSI Technology
	1Mb Non-Volatile Random Access Memory Using Oxide Semiconductor	3rd IEEE International Memory Workshop (IMW)
2012	9.2: New Threshold Voltage Compensation Pixel Circuits in 13.5-inch Quad Full High Definition OLED Display of Crystalline In-Ga-Zn-Oxide FETs	SID Symposium Digest of Technical Papers, Volume 43, Issue 1
	15.1: Research, Development, and Application of Crystalline Oxide Semiconductor	SID Symposium Digest of Technical Papers, Volume 43, Issue 1
	43.1: Low-power Display System Driven by Utilizing Technique Using Crystalline IGZO Transistor	SID Symposium Digest of Technical Papers, Volume 43, Issue 1
	27.4: 13.5-inch Quad-FHD Top-Emission OLED Display Using Crystalline-OS-FET	SID Symposium Digest of Technical Papers, Volume 43, Issue 1
	16.2: Crystalline OS-LCD Using Blue-Phase Liquid Crystal Having Characteristic Texture	SID Symposium Digest of Technical Papers, Volume 43, Issue 1
	Optical properties and evaluation of localized level in gap of In-Ga-Zn-O thin film	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Composition ratio in In-Ga-Zn-Oxide FET and photoirradiation stability	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Theoretical examination on a significantly low off-state current of a transistor using crystalline In-Ga-Zn-oxide	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	13.5-inch quarter-HD flexible AMOLED with crystalline oxide FET	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	13.5-inch quarter high definition white tandem OLED display using crystalline In-Ga-Zn-Oxide technology	19th International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Nonvolatile Memory With Extremely Low-Leakage Indium-Gallium-Zinc-Oxide Thin-Film Transistor	IEEE Journal of Solid-State Circuits
	DRAM Using Crystalline Oxide Semiconductor for Access Transistors and Not Requiring Refresh for More Than Ten Days	4th IEEE International Memory Workshop
2013	16.1: Negative-Bias Photodegradation Mechanism in InGaZnO TFT	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	52.3: Development of Back-channel-etched TFT Using C-Axis Aligned Crystalline In-Ga-Zn-Oxide	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	67.3: New Driving Method for Reducing Eye Strain Technology (REST) in Displaying Still Image Using CAAC IGZO LC Display	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	A 3.4-in. Flexible High-Resolution Full-Color Top-Emitting AMOLED Display	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	56.1: Development of IGZO-TFT and Creation of New Devices Using IGZO-TFT	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	27.1: 13.3-inch CAAC-IGZO-FET OLED Display with Narrow Driver Area Using Highly Efficient Deep Blue Device	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	28.2: Driving Method of FFS-Mode OS-LCD for Reducing Eye Strain	SID Symposium Digest of Technical Papers, Volume 44, Issue 1
	FFS-mode OS-LCD for reducing eye strain	Journal of the Society for Information Display, Volume 21, Issue 10
	Applications of crystalline Indium-Gallium-Zinc-Oxide technology to LSI: Memory, processor, image sensor, and field programmable gate array	Fifth Asia Symposium on Quality Electronic Design (ASQED 2013)
	A possibility of crystalline Indium-Gallium-Zinc-Oxide	Fifth Asia Symposium on Quality Electronic Design (ASQED 2013)
	13.5-inch Quadra-FHD flexible AMOLED with crystalline oxide FET	Twentieth International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Crystallography of In-Ga-Zn-O thin film having CAAC structure	Twentieth International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Comparison of crystal structures among CAAC-InGaZnO, nc-InGaZnO, and solution-processed InGaZnO	Twentieth International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Crystallography of excimer laser-crystallized In-Ga-Zn-O film	Twentieth International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	Analysis of nanoscale crystalline structure of In-Ga-Zn-O thin film with nano beam electron diffraction	Twentieth International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	A 3bit/cell nonvolatile memory with crystalline In-Ga-Zn-O TFT	5th IEEE International Memory Workshop
	Processor with 4.9-μs break-even time in power gating using crystalline In-Ga-Zn-oxide transistor	IEEE COOL Chips XVI
2014	44.1: Distinguished Paper: 13.3-in. 8K x 4K 664-ppi OLED Display Using CAAC-OS FETs	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	3.3: Invited Paper: Future Possibility of C-Axis Aligned Crystalline Oxide Semiconductors Comparison with Low-Temperature Polysilicon	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	21.3: A 13.5-in. Quad-FHD Flexible CAAC-OS AMOLED Display with Long-Life OLED Device Structure	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	33.1: Channel-Etched C-Axis Aligned Crystalline Oxide Semiconductor FET Using Cu Wiring	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	21.1: A 513-ppi FFS-Mode TFT-LCD using CAAC Oxide Semiconductor Fabricated by a 6-Mask Proces	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	P-9: Study of the Origin of Major Donor States in Oxide Semiconductor	SID Symposium Digest of Technical Papers, Volume 45, Issue 1
	44.3: 513-ppi Liquid Crystal Display Using C-Axis Aligned Crystalline Oxide Semiconductor with Narrow Bezel and Aperture Ratio Greater Than 50%	SID Symposium Digest of Technical Papers, Volume 45, Issue 1

Year	Titles	Papers/International Conferences
2014	Back-channel-etched thin-film transistor using c-axis-aligned crystal In-Ga-Zn oxide	Journal of the Society for Information Display, Volume 22, Issue 1
	A 513-ppi FFS-mode LCD using technique for changing part of active layer of oxide semiconductor to transparent electrode	Journal of the Society for Information Display, Volume 22, Issue 4
	A 13.5-in. Quad-FHD flexible CAAC-OS AMOLED display with long-life OLED device structure	Journal of the Society for Information Display, Volume 22, Issue 12
	Embedded SRAM and Cortex-M0 Core Using a 60-nm Crystalline Oxide Semiconductor	IEEE Micro
	Scaling to 50-nm C-axis aligned crystalline In-Ga-Zn oxide FET with surrounded channel structure and its application for less-than-5-nsec writing speed memory	Symposium on VLSI Technology (VLSI-Technology)
	A 32-bit CPU with zero standby power and 1.5-clock sleep/2.5-clock wake-up achieved by utilizing a 180-nm C-axis aligned crystalline In-Ga-Zn oxide transistor	Symposium on VLSI Circuits
	SRAM with c-axis aligned crystalline oxide semiconductor: Power leakage reduction technique for microprocessor caches	IEEE 6th International Memory Workshop (IMW)
	Embedded SRAM and Cortex-M0 core with backup circuits using a 60-nm crystalline oxide semiconductor for power gating	IEEE COOL Chips XVII
	30.9 Normally-off computing with crystalline InGaZnO-based FPGA	IEEE International Solid-State Circuits Conference (ISSCC)
2015	P-11: Channel-Etched CAAC-OS FETs using Multi-layer IGZO	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	P-13: The Relationship Between Crystallinity and Device Characteristics of In-Sn-Zn-Oxide	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	18.4: 13.3-inch 8k4k 664-ppi Foldable OLED Display Using Crystalline Oxide Semiconductor FETs	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	45.1: Invited Paper: Future Possibilities of Crystalline Oxide Semiconductor, Especially C-Axis-Aligned Crystalline IGZO	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	63.3: Fabrication of 8k4k Organic EL Panel using High-Mobility IGZO Material	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	57.3: Distinguished Paper: New Pixel Circuits for Controlling Threshold Voltage by Back-gate Bias Voltage using Crystalline Oxide Semiconductor FETs	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	70.4: A 2.78-in 1058-ppi Ultra-High-Resolution OLED Display using CAAC-OS FETs	SID Symposium Digest of Technical Papers, Volume 46, Issue 1
	An 81-in. 8K OLED Kawara-type multidisplay with flexible displays that provides a seamless image	Journal of the Society for Information Display, Volume 23, Issue 10
	Relationship between crystallinity and device characteristics of In-Sn-Zn oxide	Journal of the Society for Information Display, Volume 23, Issue 12
	13.3-inch 8k4k 664-ppi foldable OLED display using crystalline oxide semiconductor FETs	Journal of the Society for Information Display, Volume 23, Issue 12
	Fabrication of 8K4K organic EL panel using high-mobility IGZO material	Journal of the Society for Information Display, Volume 23, Issue 12
	20-nm-Node trench-gate-self-aligned crystalline In-Ga-Zn-Oxide FET with high frequency and low off-state current	IEEE International Electron Devices Meeting (IEDM)
	30-nm-channel-length c-axis aligned crystalline In-Ga-Zn-O transistors with low off-state leakage current and steep subthreshold characteristics	Symposium on VLSI Technology (VLSI Technology)
	Flexible displays using c-axis-aligned-crystal oxide semiconductors	22nd International Workshop on Active-Matrix Flatpanel Displays and Devices (AM-FPD)
	A 16-Level-Cell Nonvolatile Memory with Crystalline In-Ga-Zn Oxide FET	IEEE International Memory Workshop (IMW)
	Normally-Off Computing for Crystalline Oxide Semiconductor-Based Multicontext FPGA Capable of Fine-Grained Power Gating on Programmable Logic Element With Nonvolatile Shadow Register	IEEE Journal of Solid-State Circuits
	6.5 25.3μW at 60fps 240×160-pixel vision sensor for motion capturing with in-pixel non-volatile analog memory using crystalline oxide semiconductor FET	IEEE International Solid-State Circuits Conference - (ISSCC)
	16.9 A 128kb 4b/cell nonvolatile memory with crystalline In-Ga-Zn oxide FET using Vt, cancel write method	IEEE International Solid-State Circuits Conference - (ISSCC)
	Effect of Surrounded-Channel Structure on Electrical Characteristics of c -Axis Aligned Crystalline In–Ga–Zn–O Field-Effect Transistor	IEEE Electron Device Letters
	A Boosting Pass Gate With Improved Switching Characteristics and No Overdriving for Programmable Routing Switch Based on Crystalline In-Ga-Zn-O Technology	IEEE Transactions on Very Large Scale Integration (VLSI) Systems
2016	76-3: Development of a Top-Gate Transistor with Short Channel Length and C-Axis-Aligned Crystalline Indium-Gallium-Zinc-Oxide for High-Resolution Panels	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	60-2: A New Concept of In-Ga-Zn Oxide Composition for Fabricating High Mobility and Stability FETs	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	P-52: Morphological and Electrical Difference in C-axis Aligned Crystalline IGZO Films Based on the Sputtering Method	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	76-1: Invited Paper: CAAC-IGZO Technology	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	P-4: Electrical Characteristics of Dual-Gate CAAC-IGZO FET with Self-Aligned Top Gate	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	78-4: Distinguished Paper: A 2.78-in 1058-ppi Ultra-High-Resolution Flexible OLED Display Using CAAC-IGZO FETs	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	69-3: 806-ppi 4K2K LC Display using Top-gate Self-aligned CAAC-OS FET	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	7-1: Distinguished Paper: 13.3-inch 8k4k 664-ppi 120-Hz 12-bit OLED Display Using Top-Gate Self-Align CAAC-OS FETs and 12-bit Source Driver IC	SID Symposium Digest of Technical Papers, Volume 47, Issue 1

Year	Titles	Papers/International Conferences
2016	P-143: Fabrication of 5.5-inch 4K2K Liquid Crystal panel using High-mobility IGZO Material	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	37-2: 1058-ppi 4K LC Display Using a Top-Gate Self-Aligned CAAC-OS FET	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	P-26: A 1058 ppi 8K4K OLED Display using a Top-Gate Self-Aligned CAAC Oxide Semiconductor FET	SID Symposium Digest of Technical Papers, Volume 47, Issue 1
	New pixel circuits for controlling threshold voltage by back-gate bias voltage using crystalline oxide semiconductor FETs	Journal of the Society for Information Display, Volume 24, Issue 1
	Ultra-high-resolution 1058-ppi OLED displays with 2.78-in size using CAAC-IGZO FETs with tandem OLED device and single OLED device	Journal of the Society for Information Display, Volume 24, Issue 3
	Extremely low power c-axis aligned crystalline In-Ga-Zn-O 60 nm transistor integrated with industry 65 nm Si MOSFET for IoT normally-off CPU application	IEEE Symposium on VLSI Technology
	Embedded memory and ARM Cortex-M0 core using 60-nm C-axis aligned crystalline indium-gallium-zinc oxide FET integrated with 65-nm Si CMOS	IEEE Symposium on VLSI Circuits (VLSI-Circuits)
	A 25. 3 μ W at 60 fps 240×160 Pixel Vision Sensor for Motion Capturing With In-Pixel Nonvolatile Analog Memory Using CAAC-IGZO FET	IEEE Journal of Solid-State Circuits
2017	P-7: A 65-in. 8K LCD and OLED Display Using Cloud-Aligned Composite Oxide-Semiconductor (CAC-OS) FET	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	76-2: Field-Effect Transistor with CAAC/CAC-OS Double-Layer Structure for Diversion of Gen 8-10.5 Amorphous Silicon Production Lines	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	42-2: Low Power Consumption 8K Liquid Crystal Display with Oxide Semiconductor/Oxide Conductor Pixel (Transparent Pixel)	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	24-1: Invited Paper: Flexible OLED Display Using C-Axis-Aligned-Crystal/Cloud-Aligned Composite Oxide Semiconductor Technology and Laser Separation Technology	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	P-48: An Oxide-Semiconductor (OS) FET-based Low-Power Level Shifter Combined with OS LSI Technology-based Display-Controller COG for a Low-Power OS Display System	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	63-2: A Novel Touch-control Method with Partial Scanning for LC, OLED, and Hybrid Displays using an Oxide Semiconductor	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	18-5: A 1058-ppi 4K Ultrahigh-Resolution and High Aperture LCD with Transparent Pixels using OS/OC Technology	SID Symposium Digest of Technical Papers Volume 48, Issue 1
	77-4: A 2.78-in 1058-ppi Ultra-High-Resolution OLED Hybrid Display using Oxide Semiconductor/Oxide Conductor (OS/OC) Pixel (Transparent Pixel) achieving High Aperture Ratio	SID Symposium Digest of Technical Papers, Volume 48, Issue 1
	Performance boost of crystalline In-Ga-Zn-O material and transistor with extremely low leakage for IoT normally-off CPU application	Symposium on VLSI Circuits
	A 140 MHz 1 Mbit 2T1C gain-cell memory with 60-nm indium-gallium-zinc oxide transistor embedded into 65-nm CMOS logic process technology	Symposium on VLSI Circuits
	Embedded Memory and ARM Cortex-M0 Core Using 60-nm C-Axis Aligned Crystalline Indium–Gallium–Zinc Oxide FET Integrated With 65-nm Si CMOS	IEEE Journal of Solid-State Circuits
	Subthreshold Operation of CAAC-IGZO FPGA by Overdriving of Programmable Routing Switch and Programmable Power Switch	IEEE Transactions on Very Large Scale Integration (VLSI) Systems
2018	50-3: Formation of Source and Drain Regions in Top-Gate Self-Aligned Oxide Semiconductor Field-Effect Transistor	SID Symposium Digest of Technical Papers, Volume 49, Issue 1
	46-4: 513-ppi Hybrid Display with Stacked Transistors	SID Symposium Digest of Technical Papers, Volume 49, Issue 1
	High thermal tolerance of 25-nm c-axis aligned crystalline In-Ga-Zn oxide FET	IEEE International Electron Devices Meeting (IEDM)
	A 20ns-write 45ns-read and 1014-cycle endurance memory module composed of 60nm crystalline oxide semiconductor transistors	IEEE International Solid - State Circuits Conference - (ISSCC)
2019	23-1: Distinguished Paper: 5291 ppi Organic Light Emitting Diode Display using Field-effect Transistors Including a C-Axis Aligned Crystalline Oxide Semiconductor	SID Symposium Digest of Technical Papers, Volume 50, Issue 1
	23-2: 2351-ppi OLED Display with Stacked OS-FETs with L = 0.36 μm	SID Symposium Digest of Technical Papers, Volume 50, Issue 1
	37-1: Liquid Crystal Display Panel with a Pixel Including Oxide Semiconductor Field-Effect Transistor Memory (Pixel AI)	SID Symposium Digest of Technical Papers, Volume 50, Issue 1
	A 5291-ppi organic light-emitting diode display using field-effect transistors including a c-axis aligned crystalline oxide semiconductor	Journal of the Society for Information Display, Volume 27, Issue 8
	3D-Stacked CAAC-In-Ga-Zn Oxide FETs with Gate Length of 72nm	IEEE International Electron Devices Meeting (IEDM)
	An Energy-Efficient Normally Off Microcontroller With 880-nW Standby Power, 1 Clock System Backup, and 4.69- μ s Wakeup Featuring 60-nm CAAC-IGZO FETs	IEEE Solid-State Circuits Letters
	A 48 MHz 880-nW Standby Power Normally-Off MCU with 1 Clock Full Backup and 4.69-μs Wakeup Featuring 60-nm Crystalline In–Ga–Zn Oxide BEOL-FETs	Symposium on VLSI Circuits
	A c-Axis-Aligned Crystalline In-Ga-Zn Oxide FET With a Gate Length of 21 nm Suitable for Memory Applications	IEEE Journal of the Electron Devices Society
	12.2 Micro Short-Circuit Detector Including S/H Circuit for 1hr Retention and 52dB Comparator Composed of C-Axis Aligned Crystalline IGZO FETs for Li-Ion Battery Protection IC	IEEE International Solid- State Circuits Conference - (ISSCC)

Year	Titles	Papers/International Conferences
2020	21-1: Invited Paper: 5291-ppi Microdisplay Using CAAC-IGZO FET with Channel Length of 60 nm	SID Symposium Digest of Technical Papers, Volume 51, Issue 1
	Hydrogen Absorption Method Using HfOx in Crystalline In-Ga-Zn Oxide FETs for NVM Applications	IEEE International Electron Devices Meeting (IEDM)
2021	P-4: Novel Oxide Semiconductors Enabling as High On-State Current as LTPS	SID Symposium Digest of Technical Papers, Volume 52, Issue 1
	9-4: Fabrication of Oxide-Semiconductor FETs with Submicron Channel Length	SID Symposium Digest of Technical Papers, Volume 52, Issue 1
	Novel Analog in-Memory Compute with > 1 nA Current/Cell and 143.9 TOPS/W Enabled by Monolithic Normally-off Zn-rich CAAC-IGZO FET-on-Si CMOS Technology	IEEE International Electron Devices Meeting (IEDM)
	Source/Drain Engineering by Tantalum Nitride (TaNx) Electrode for Boosting OSFET Performance	IEEE International Electron Devices Meeting (IEDM)
	A Compact Physics-Based Charge Core Model for CAAC In-Ga-Zn Oxide Multi-Gate FETs	5th IEEE Electron Devices Technology & Manufacturing Conference (EDTM)
2022	P-6: Student Poster: 2731ppi OLED Display with Low Power Consumption and Wide Viewing Angle Using OS/Si VLSI Process Technology	SID Symposium Digest of Technical Papers, Volume 53, Issue 1
	27-1: Fabrication Method for Miniaturized CAAC-OS FET for High-Definition AR/VR Displays	SID Symposium Digest of Technical Papers, Volume 53, Issue 1
	P-8: Analysis of Degradation Mechanism of Oxide Semiconductor FETs with High Tolerance to Intense NBTIS	SID Symposium Digest of Technical Papers, Volume 53, Issue 1
	32-3: 1.5-inch, 3207-ppi Side-by-Side OLED Display Capable of 32-Division Driving with OSLSI/SiLSI Structure Fabricated by Photolithography	SID Symposium Digest of Technical Papers, Volume 53, Issue 1
	10-1: Layout of 1.50-inch, 3207-ppi OLED Display with OSLSI/SiLSI Structure Capable of Division Driving Fabricated through VLSI Process with Side-by-Side Patterning by Photolithography	SID Symposium Digest of Technical Papers, Volume 53, Issue 1
	5,291-ppi OLED display enabled by monolithic integration of C-axis-aligned crystalline IGZO FET and Si CMOS	Journal of the Society for Information Display, Volume 30, Issue 9
	Physics-Based Compact Model for CAAC In-Ga-Zn Oxide Multi-Gate FETs with Free Shape of Fin	6th IEEE Electron Devices Technology & Manufacturing Conference (EDTM)

SEL has announced a proprietary material technology called CAAC-IGZO, the main points of which are described below. (CAAC® is a registered trademark of SEL, No. 5473530.) As described in Chapter 6, on June 1, 2012, SEL and Sharp jointly announced a new microcrystalline channel material[77] for oxide transistors called CAAC® (C-Axis Aligned Crystal), which has the same elements and similar composition ratio as the amorphous $InGaZnO_4$ discovered by Hideo Hosono et al. The SEL website mentions "SEL discovered a crystal structure with c-axis alignment in a direction perpendicular to the film surface and without alignment in the a-b plane (CAAC®), in a crystalline oxide semiconductor thin film formed at temperatures lower than 450ºC." By analogy with this description, can we think of this channel film as a complex of nanosized-crystalline particles with their c-axis approximately perpendicular to the film surface? This crystalline CAAC-IGZO technology[34), 41), 61), 75), 76)] has the following characteristics: (1) good saturation characteristics and current controllability, (2) low off-current, (3) high withstand voltage, (4) downsizing and highspeed operation and (5) stack of Si sand CAAC-OS is possible. The SEL company has made many technical presentations in collaboration with Sharp based on this system.

Furthermore, in 2016, the SEL group seems to have found another material phase suitable for a channel layer. It is a new thin film phase, which is the same InGaZnO system, but 2-3 nm sized crystals with phase separation in the thin film by adjusting the target composition. SEL has named it "Cloud-Aligned Composite oxide semiconductor. [46), 79)]" Whether it is "CAAC-IGZO" or "Cloud-Aligned Composite", the author can assume that Sharp and SEL have already overcome the challenges of TFT quality and mass production, since many products using TFTs with these materials as channels have been introduced to the market.[80)-85)]

In this way, SEL was quick to capture the essence of Hosono's original IGZO-TFT technology (both amorphous IGZO and crystalline IGZO), and in collaboration with Sharp, is boldly taking on the challenge of not only developing transistor technology and panel technology, but also the memory field. SEL is believed to be working with Sharp to develop this product at an extremely rapid pace. Furthermore, the CAAC-IGZO technology seems to be spreading to a research team at Hanyang University in South Korea, whose group is also promoting research on flash memory applications, etc., which is very interesting[86), 87)]. The details of these distinctive technologies of SEL are also described in the book "Physics and Technology of Crystalline Oxide Semiconductor CAAC-IGZO" (3 books in the series)[88)], which was supervised and written by President Shunpei Yamazaki.

7.3.2 Novel High Performance IGZO-TFT Composed of In/Ga Compositional Modulated Channel Structure with High Mobility and High Photostability

Since its publication in Nature by Hideo Hosono, "IGZO -TFT" technology has caused a major upheaval in the electronics industry. "IGZO" was the most promising candidate as a channel semiconductor material for next-generation TFTs to replace amorphous silicon in the industrial world, and research and development of IGZO from various angles, such

as manufacturing technology for large-area TFT devices and improving the stability of transistor devices, have taken off in a big way. Under such circumstances, one of the remaining issues for IGZO-TFTs is the problem of disturbance by visible light, especially blue light. At the end of 2011, Fujifilm Corporation (hereafter referred to as Fujifilm) announced an original multilayer amorphous oxide semiconductor transistor with extremely small disturbance behavior and a mobility that is four times higher than normal[89].

Fujifilm's Frontier Core-Technology Laboratories group first appeared in this IGZO-based TFT field at the 57th JSAP Spring Meeting 2010 (Tokai University). They were greatly inspired by a series of transistors using IGZO-based oxide semiconductors developed by Hideo Hosono, a professor at the Tokyo Institute of Technology, and carried out five presentations[90] at that JSAP meeting, ranging from physical properties of IGZO to characteristics of TFT devices, including a follow-up to the research results of Hosono's group. Fujifilm's energetic activities were featured in an article in the Nihon Keizai Shimbun (Japanese newspaper) on March 27, 2010.

The Fujifilm research group was then convinced that the amorphous IGZO-TFT created by Hosono would be a strong candidate for the next generation of transistors, and they narrowed their focus to two issues, further increasing the mobility of IGZO and improving its stability in visible light (especially blue wavelengths), and they have concentrated on the development of channel materials that would simultaneously satisfy these two challenges. As a result, Fujifilm's group created an advanced amorphous oxide semiconductor channel with two layer stacked structure and presented[89] that this channel structure was a high-performance device with high mobility exceeding 40 cm^2/Vs, which was one of the highest in the world at that time, and also resolves the characteristic fluctuations such as threshold voltage under light irradiation, which was a weak point of a-IGZO TFTs, at the 18th International Display Workshops (IDW 2011) held in December 2011.

Though at that time, there were several reports[91), 92)] attempting to use a bilayer structure such as [InZnO or InSnO]/InGaZnO or InSnO/ZnSnO for the channel structure of oxide semiconductors, a major problem remained: degradation of device characteristics due to light irradiation,[93), 94)] which had been a concern for some time. Kenji Nomura et al. in Hosono's group pointed out, through detailed analytical experiments, that this problem may be caused by oxygen defects that easily occur at the interface between the gate oxide layer and channel layer[95]. Masashi Ono and Masahiro Takata et al. of Fujifilm's Frontier Core-Technology Laboratories thought that since amorphous IGZO is an oxide, semiconducting properties would be greatly affected by oxygen defects, and investigated oxygen diffusion into amorphous oxide thin films in detail using the isotope ^{18}O. The results showed that oxygen diffuses into amorphous oxide thin films to a depth of 15 nm at 450°C. The oxygen diffusion at each temperature is shown in Fig. 7.10.

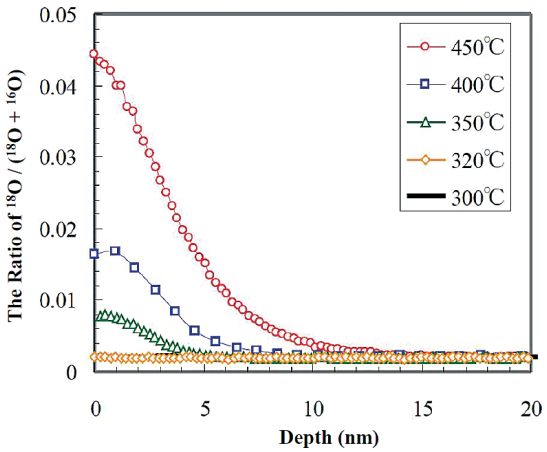

Fig. 7.10 Diffusion profiles of oxygen isotope ^{18}O in amorphous IGZO films at various temperatures.
(Published the figure in reference (89) revised a little by courtesy of Dr. Masashi Ono.)

Based on the oxygen diffusion data, a 5-nm thick $In_{1.85}Ga_{0.15}ZnO_4$ film with In-rich and Ga-poor composition was formed as the first layer on top of the SiO_2 layer, which is a bottom-gate type gate thermal oxide, as the main carrier transport layer with high carrier density, and formed sequentially a second $In_{0.5}Ga_{1.5}ZnO_4$ film with In-poor and Ga-rich composition was formed as the high resistivity layer on the first layer. At this stage, the thickness of this high resistivity layer was fixed at 8 nm and sufficient oxygen diffusion was performed from the high-resistance layer side through the main carrier transport layer to the gate oxide film interface by annealing at 450ºC in a dry oxygen atmosphere. This process is part of a design concept in which defects likely to be present at the interface between the gate oxide film and the channel layer are drastically reduced. Then, a high resistance layer with the same In/Ga composition was additionally stacked so that the overall film thickness was 50 nm. The structure of this two-layer stacked channel is shown in Fig. 7.11. The electrodes are Ti/Au (10 nm/40 nm).

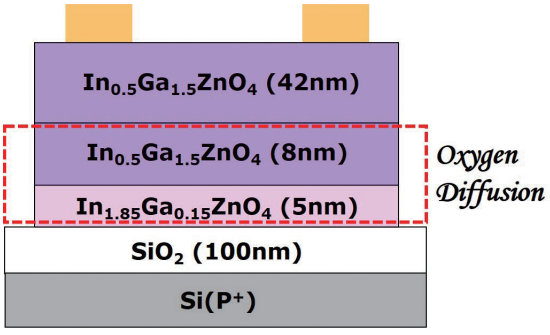

Fig. 7.11 The best structure of stacked amorphous IGZO-TFTs with high mobility and stable to light irradiation, optimized as a result of oxygen diffusion data and exploration of In/Ga composition ratios
(Published the figure in reference (89) revised a little by courtesy of Dr. Masashi Ono.)

With this two-layer stacked channel transistor, electron mobility of 41.8 cm^2/Vs was achieved, and furthermore, the Vth shift (ΔVth) was very successfully stabilized at about −0.04 V even under irradiation in the blue wavelength range of λ = 400 nm. Fig. 7.12 shows the Vgs-Ids characteristics of each transistor at different light irradiation wavelengths.

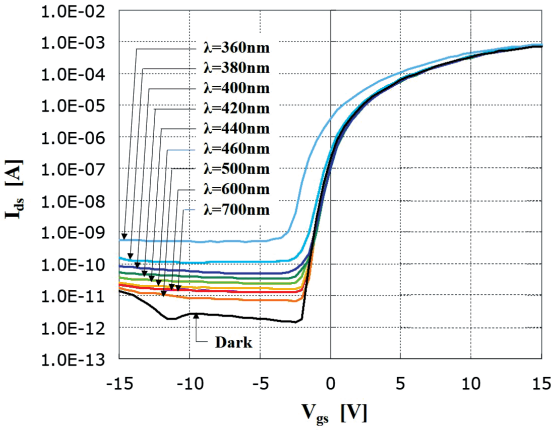

Fig. 7.12 V_{gs}-I_{ds} characteristics of stacked amorphous IGZO-TFTs.
(Published the figure in reference (89) revised a little by courtesy of Dr. Masashi Ono.)

The following four factors can be considered behind the achievement of this challenging goal. (1) The In-Ga-Zn-O system is not impurity-doped but a material whose conductivity (carrier density) can be largely controlled by the composition ratio between In and Ga, (2) Advanced nano-scale deposition technology during oxide channel layer fabrication, (3) The fact that the constituent elements hardly diffused during post-annealing (good luck), (4) Precise oxygen control technology by diffusion. This success can be attributed to the appropriate integration of all these technologies.

In order to discuss the In/Ga composition-modulated multilayer film, which was a major factor in the achievement of this multilayer transistor technology, a sample of five-layer stacked IGZO-based oxide semiconductor thin film with composition-modulated In/Ga ratio was prepared on a quartz glass substrate. The HAADF-STEM (High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy) image of the cross section of the sample is shown in Fig. 7.13.

The research presentation by Masashi Ono et al. at IDW 2011 attracted a great deal of attention and was featured in an article on Tech-on (now Nikkei Cross Tech), a technical information website at the time[96]. In addition, the following year, Ono gave an invited lecture at an international conference (IMID 2012=The 12th International Meeting on Information Display) held in Korea based on the results of this research[97].

Due in part to this accumulation of technology, Fujifilm's patents related to IGZO-based oxide TFT had once held the top position in the "Ranking of Capability to Prevent Other Companies from Obtaining Rights Using Patents in the Chemical Industry" announced by Patent Result Co., Ltd. for multiple years[98].

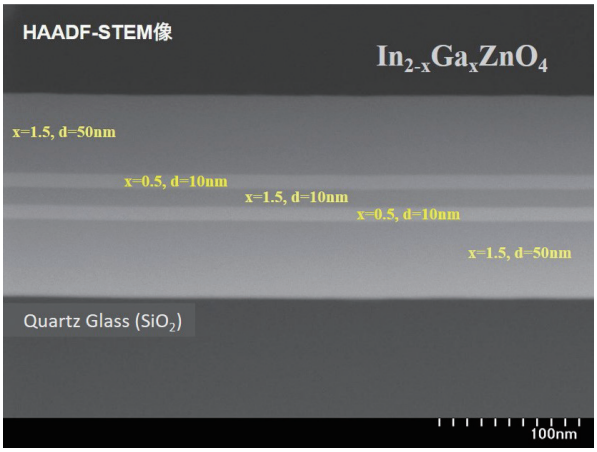

Fig. 7.13 Cross-sectional HAADF-STEM image of a 5-layer stacked IGZO-based amorphous oxide semiconductor thin film with modulated In/Ga composition ratio.
Masahiro Takata and Masashi Ono kindly provided the author with the photographic originals described in four registered patents (Patent No. 5497417, Patent No. 5626978, Patent No. 5901420, and Patent No. 5052693) with the composition X value of each layer and its thickness specified.

7.3.3 Growth of $InGaZnO_4$ Bulk Single Crystal

In 2019, a joint research team led by Nobuaki Miyakawa, a professor of Tokyo University of Science and Noboru Kimizuka, a visiting professor of the University of Sonora, Mexico, succeeded in single crystal growth of bulk $InGaZnO_4$, which is attracting attention as a transparent oxide semiconductor material, using the Floating Zone (FZ) method. This achievement was published in a specialized journal[99]. Unlike the previous 3 examples[100-102] reported on $InGaZnO_4$ single crystals, they managed to grow large bulk single crystals in the scale of centimeters. Most research on this material system is on its material properties as a thin film. Previous studies include 0.02x0.1x0.1cm^3 fragments of $InGaO_3(ZnO)_3$ single crystals by Kimizuka et al.[100] during his days at NIMS, and sintered polycrystalline ceramics by Moriga et al.[103] from Tokushima University and Orita et al.[104] from HOYA. However, no reports have been published on centimeter-scale bulk single crystals, as reported by Miyakawa. The understanding and elucidation of fundamental physical properties using bulk single-crystal materials is highly valuable for further improving thin-film transistor characteristics in the future. The report by Miyakawa et al. on growing large bulk single crystals holds significant importance in this regard.

Since Miyakawa et al. use "IGZO-mn" to express the general chemical formula $(InGaO_3)_m(ZnO)_n$ (m, n = natural numbers), $InGaZnO_4$ is expressed as "IGZO-11". IGZO-11 single crystals grown using the FZ method have a somewhat deep blue hue in the as-grown state. However, post-annealing heat treatment in an oxygen atmosphere turns the single crystals remarkably transparent, as shown in Fig. 7.14.

Additionally, Miyakawa et al. measured the temperature dependence of electrical properties. They confirmed that annealing in an oxygen atmosphere allows the carrier density and electrical conductivity to be controlled within the range

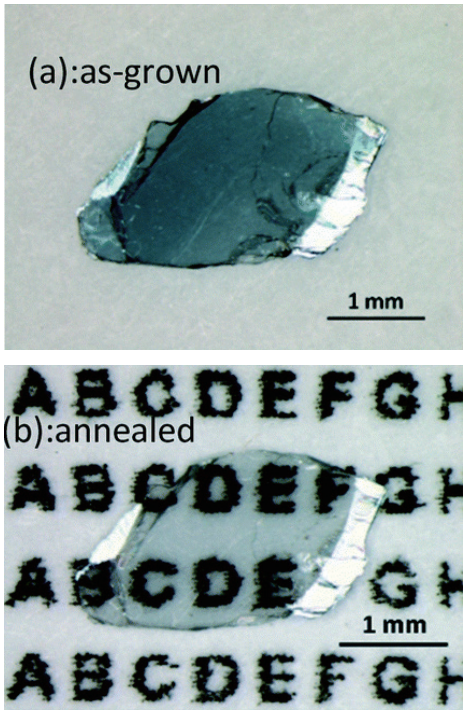

Fig. 7.14 Photograph of $InGaZnO_4$ (IGZO-11) single crystal[99].
(a) Photograph of as-grown single crystal.
(b) Photograph of the single crystal after annealing at 1000°C for 72 hours in O_2 gas flow. The thickness of a single crystal is 0.195 mm.
(Reprinted with permission from the Royal Society of Chemistry.)

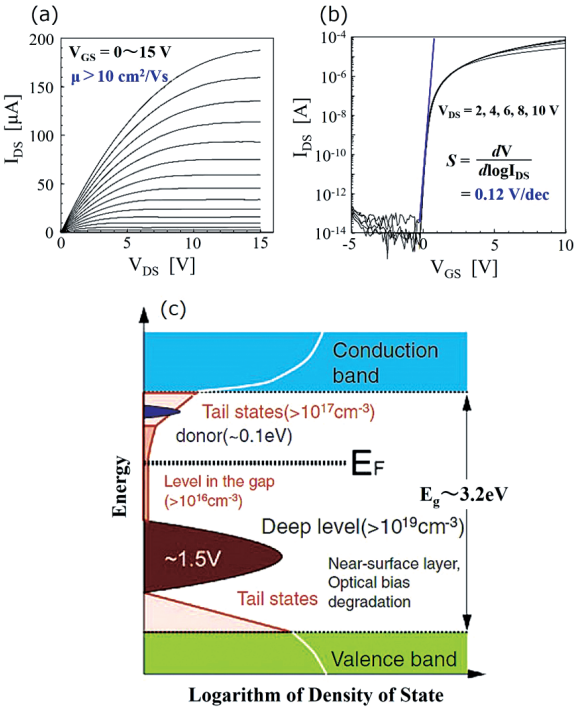

Fig. 7.15 Electronic structure and electronic TFT-characteristics of amorphous IGZO (a-IGZO).
(a) Output characteristics with gate voltage as a parameter (Drain current dependence on drain voltage with gate voltage as a parameter). The electron mobility calculated from the saturation region is higher than 10 cm^2/Vs.
(b) Transfer characteristics (The gate voltage dependence of the drain current flowing between the source and drain under constant drain voltage). The S-value (S.S.: Subthreshold swing) is a small value that is not a problem for TFT.
(c) Electronic structure (Band diagram) of a-IGZO. The vertical axis represents the energy of the electrons, and the horizontal axis represents the density of states of the electrons schematically as an image.
(Published three figures in reference (118) revised a little by courtesy of Prof. Hosono.)

of $7x10^{17}cm^{-3}$ to $6x10^{19}$ cm^{-3} and 1 S/cm to 2000 S/cm, respectively. They also confirmed that mobility increases as the carrier density increases, which is consistent with the research results of Nomura et al.[105)-107)], suggesting it to be an intrinsic physical property of IGZO-based materials. Furthermore, the team clarified that the electrical conductivity σ_c along the c-axis of the single crystal is significantly smaller than the electrical conductivity σ_{ab} in the ab-plane. Subsequently, Miyakawa et al. succeeded in growing single crystals from IGZO-11 to IGZO-19 and confirmed that the optical gap (Tauc gap) decreases monotonically as the n-value increases[108)]. This trend is consistent with the shift towards longer optical absorption wavelengths observed with the increase in ZnO layers, as reported by Moriga et al.[103)].

Knowing the exact value of the anisotropy of electrical conduction in bulk single crystals is extremely useful for considering future application devices. I am confident that we will see further improvement in the performance of oxide transistors as various physical properties are clarified in the future.

7.3.4 Subsequent Research Developments by The Hosono Group

The Hosono group subsequently conducted various studies to explore the nature of a-IGZO and published Fig. 7.15 (a), (b), (c)[109-120)], which show transistor characteristics of a higher quality and band structure showing detailed electronic state than in 2004.

One of the characteristics of a-IGZO TFTs is the extremely low off-current that flows when a negative gate voltage is applied. (The value is several orders of magnitude lower than a-Si.). This is believed to be due to localized levels derived from oxygen defects, which have a much higher density near the valence band maximum (VBM) than near the conduction band minimum (CBM). This characteristic of the a-IGZO transistor is one aspect that makes it a good material for display drive applications since it suppresses leakage current, leading to lower power consumption. Significant issues can arise in current-controlled organic light-emitting diode (OLED) displays if the characteristics change under the application of negative bias during light irradiation. Therefore, it is considered that the localized levels near the VBM are appropriately adjusted by adjusting the moisture content and oxygen partial pressure when fabricating thin films.

I would like to briefly mention a few of the research results that caught my attention from the subsequent studies by the Hosono group. One of them is a TFT with a two-layer stacked channel structure of ITZO (=$InSnZnO_x$) [20 nm]/IGO (= $InGaO_x$) [15 nm], developed by a group led by Junghwan

Kim, Assistant Professor at the Tokyo Institute of Technology's Materials Research Center for Element Strategy, and the Center's Director, Hideo Hosono and his group, to solve the trade-off problem between mobility and stability[121].

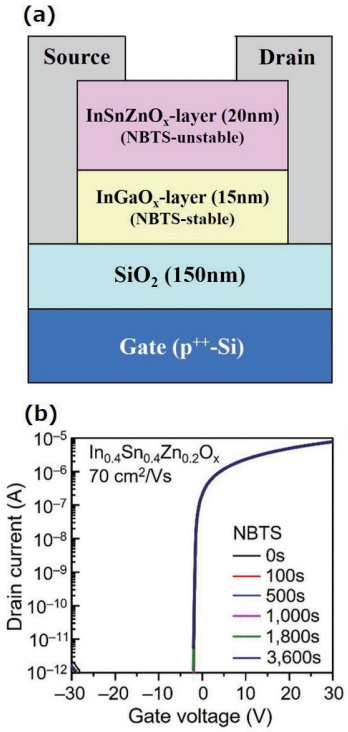

Fig. 7.16 The TFT with a new two-layer stacked channel structure that greatly improves the mobility and stability trade-off problem.
(a) Image of its TFT configuration.
(b) Transistor characteristics showing negative-bias temperature stress (NBTS) stability as an example of typical characteristics.
(Published two figures in reference (121) revised a little by courtesy of Prof. Hideo Hosono.)

In-Sn oxide TFTs exhibit high mobility and cannot be used in current-driven OLEDs because prolonged, repeated use causes a shift in the threshold voltage, resulting in significant changes in drain current values at the same gate voltage. To clarify whether the cause of the shift was a charge trap occurring in the gate insulator or changes in carrier density of the semiconductor layer forming the channel, the group fabricated a transistor with a stacked structure comprising an In-Ga-O layer that is stable under Negative Bias Temperature Stress (NBTS) and an In-Sn-Zn-O layer that is unstable under NBTS, as shown in Fig. 7.16 (a), and performed analysis by comparing with device simulations. The analysis determined that the cause of the shift was not the charge trap in the gate insulator but the increase in carrier density in the high-mobility InSnZnO layer. Furthermore, they also identified that this increase in carrier density was due to the carbon impurities (CO) produced during the semiconductor lithography process. In other words, carrier electrons are supplied from the residual impurity CO to the oxide channel layer by applying a negative bias. Since a-IGZO with mobility of around 10 cm^2/Vs does not receive this supply of carrier electrons, the threshold remains stable initially. This is because the position of the CBM is significantly lowered due to the introduction of Sn, etc., which facilitates the supply of carrier electrons. Through such meticulous analysis of transistor characteristics and the removal of carbon impurities, which was the root of the problem, the group was able to achieve TFT characteristics with high threshold stability (in this case, NBTS stability characteristics), as shown in Fig. 7.16 (b).

The essence of this paper in *Nature Electronics* goes beyond the excellence of this two-layer amorphous oxide channel structure and lies in identifying the cause of NBTS using this two-layer channel as a model for device simulations. The experimental concept was also well thought out, making this an outstanding research result. The essential content of this achievement should provide extremely important information for the industrial sector. With an electron mobility of around 70 cm^2/Vs and having solved the problem of threshold instability caused by repeated usage, amorphous oxide semiconductor TFTs now offer the possibility of large-area application due to their amorphous nature, further solidifying the impression that amorphous oxide semiconductor TFTs can sufficiently surpass Low-Temperature Polysilicon (LTPS) TFTs in achieving large-screen and high-resolution displays.

A separate paper on the impurity carbon derived during the transistor fabrication process, which is the cause of the instability mentioned above, was published by the Hosono group around the same time[122]. The paper indicates the importance of development from an overall perspective for both materials and device fabrication processes, providing valuable insights.

Another study is the fabrication of SnO-TFT[123], a p-type oxide semiconductor transistor and a demonstration of how doping with Sb can convert it to n-type, thereby imparting pn-bipolarity properties[124),125]. First, the field-effect mobility of SnO-TFT epitaxially fabricated on YSZ single-crystal substrates with highly controlled oxygen partial pressure during deposition was higher than 1 cm^2/Vs for p-type oxide semiconductor transistors. In addition, it was discovered that doping with 8% Sb or higher reverses the polarity, making it n-type. Furthermore, the clear rectification characteristics observed in the homojunction are also considered an extremely important development from the perspective of exploring functionality in materials. This series of research is significant as it has provided insight into the prospect of constructing important CMOS circuits using only oxide semiconductors, representing the opening of another significant door in oxide electronics. The field of p-type oxide semiconductors is expected to see further development. Review articles on p-type oxide transistors have been published recently[126-128], indicating the steady propagation of new material technologies pioneered by Hosono across the globe.

7.3.5 Technology Spread to Researchers Worldwide and its Trend

Eighteen years have passed since Hideo Hosono's "discovery and invention of transparent amorphous oxide semiconductor IGZO". Looking back, it remains a significant material innovation that brought about a revolution for electronics manufacturers worldwide. As previously discussed, typical practical application examples include large flat-panel displays and smartphones that use high-definition OLED screens. These are produced by display companies in Japan and countries like South Korea, Taiwan, and China. In addition, the significance of the discovery and invention of IGZO is that it has instilled a great sense of anticipation among materials researchers worldwide that "'even if oxides are used instead of Si, by carefully controlling various factors during fabrication, it might be possible to create devices that are equivalent to, or even surpass, Si". The standard set high by Hosono has been accepted by prominent researchers worldwide. Through their perspective, they have explored unique second or third paths for materials, leading to numerous new directions in research[129-182]. The applications of this extend beyond just display TFTs. This material and TFT technology have also permeated and spread to memory applications in electronics, biotechnology and medicine fields. In particular, the development of medical X-ray imaging devices has picked up in recent years[183-196]. Furthermore, research reports on the applications of "IGZO-TFT", first introduced in 2004, to X-ray flat panels are actively published[197-213].

The creation of amorphous IGZO is a typical example of how, once a major innovation is made in semiconductor materials, the core of electronics, the wave gradually becomes larger and larger and spreads steadily throughout the world.

Undoubtedly, further advancements and improvements will continue, leading to the development of even more precise and intricate devices. These technologies will ultimately contribute to creating a richer living environment for everyone. I do not doubt that Hideo Hosono, the pioneer of "IGZO", is more hopeful than anyone else for that to happen.

Methodology for Surveying Trends in IGZO-Related Papers

Although this is the author's original approach as a materials researcher, the population to be surveyed regarding contributed papers and presentations at international conferences was set as (i) through (iv) in the following four ways and examined based on what can be extracted from the data from 2005 to September 2022 (i.e., at the time of the survey).

(i) To understand the basic research status of materials from an international perspective
- Target Paper Groups: *Applied Physics Letters, Journal of Applied Physics, AIP Advances*
- URL surveyed: https://aip.scitation.org/search/advanced (Viewed on 09.26.2022)

(ii) To understand trends in materials research at a higher level of research standards
- Target Paper Groups: *Advanced Materials, Advanced Functional Materials,Advanced Electronic Materials, Advanced Materials Interfaces,Advanced Optical Materials, Advanced Materials Technologies, Advanced Science, Small*
- URL surveyed: https://onlinelibrary.wiley.com/search/advanced?publication=15214095&text1= (Viewed on 09.26.2022)

(iii) To understand the development in the flat panel/flexible display field, etc.
- Target International Conferences and Papers Group: *SID, J. Soc. Inform. Display*,
- URL surveyed: https://sid.onlinelibrary.wiley.com/search/advanced?publication=19383657&text1= (Viewed on 09.28.2022)

(iv) To understand the development of applications for semiconductor devices, circuits, sensors, display element technologies, etc.
- Target International Conferences and Papers Group: *IEEE Electron Device Letters, IEEE Trans.Electron Dev., J. Display Technol., AM-FPD, IEDM, ISSCC, VLSI Symposium,* etc.
- URL surveyed: https://ieeexplore.ieee.org/search/advanced (Viewed on 09.27.2022)

In addition, for the technical keyword search used in each of the surveys (i) through (iv), the following long keyword condition sentences were used, based on the author's experience, in order to avoid omissions in the search for the titles of papers and international conference presentations as much as possible.

◎ Keywords used in the survey
"IGZO" OR "InGaZnO" OR "InGaZn" OR "InGaZnO4" OR "GaInZnO" OR "GaInZn" OR "GIZO" OR "In-Ga-Zn-O" OR "In-Ga-Zn" OR "Ga-In-Zn-O" OR "Ga-In-Zn" OR "indium-gallium-zinc-oxide" OR "indium-gallium-zinc" OR "gallium-indium-zinc- oxide" OR "gallium-indium-zinc" OR "caac" OR "cac-os" OR "InGaO3(ZnO)" OR "transparent-amorphous-oxide-semiconductor" OR "amorphous-oxide-semiconductor" OR "oxide-based thin film transistor"

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- 2019: Develops 5th-generation IGZO, an evolution of Sharp's display core technology
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200) K. Shimazoe, A. Koyama, H. Takahashi, T. Shindoh and H. Miyoshi: "Prototype of IGZO-TFT preamplifier and analog counter for pixel detector", J. Instrumentation, 12, C02045 (2017).
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8 Summary

The primary focus of this systematic survey report was to elucidate the technological history behind amorphous oxide semiconductor transistors and reveal the genealogy of their materials research. When silicon semiconductors flourished in the world, Hideo Hosono formulated a Working Hypothesis based on the results of three experiments and delivered a lecture on the utility of amorphous oxides at a prominent international conference but received little response. He continued to believe in his "idea" despite facing such criticism. In addition, factors such as the fact that he was fortunate to have talented young researchers at the start of his research project and that as the research director, he is believed to have engaged in communication and mutual understanding of technical content within the project, all had a positive impact leading to the "crystallization" of research results in the form of the two papers published in *Science* in 2003 and in *Nature* in 2004.

In addition, efforts far beyond the scope of typical university duties were the major contributing factor behind this innovation, such as filing patent applications in Japan and overseas with the support of many experts at appropriate timings during the discovery and invention period and personal visits within Japan and overseas to explain the originality of the technology during the subsequent process of acquiring and maintaining intellectual property rights. Given that many electronics manufacturers today utilize amorphous IGZO-TFTs, the fact that the basic patents for oxide thin film transistors have been securely held in cooperation with the Japan Science and Technology Agency (JST) is undoubtedly an important foundation for considering the practical application of this technology.

In materials science, Hideo Hosono's series of conceptual processes, in which he discovered the path to practical application by choosing "amorphous" instead of "crystalline", were truly ingenious. Only Hosono, who has long been immersed in the material science of "glass", believed this was possible. Since Hosono's publication in *Nature* in 2004, I imagine that R&D personnel at many companies planning to commercialize a-IGZO must have spent several years checking and confirming "whether a-IGZO is genuine". By around 2008, several years later, they must have obtained the assurance that "IGZO was genuine and can be guided towards industrialization". Since then, a huge wave of new research and development related to IGZO began to spread from researchers worldwide, and even today, that wave continues to expand. The seeds of a-IGZO produced by Hosono have been acknowledged by many researchers around the world, who took the seeds home to their respective fields, cultivated them, and are now on the verge of yielding new fruit. IGZO thin films are already in commercial use, and the IGZO technology is spreading far beyond the initial expectations, including displays, applications in memory, X-ray detectors in the medical field, and biosensors. Once IGZO technology is recognized as a technology that can be mass-produced by companies, it is used in a variety of fields, and the speed at which it is spreading is truly remarkable.

Hosono, on the other hand, created from scratch the seeds of a technology that no one had ever tried before and chewed through at least seven to eight years of hardship before other R&D people understood the significance of his work. Although it is not impossible to understand the atmosphere in which Hosono is called "a person thinking outside the box," the author feels that Hosono has a strong core that will not yield to anything, which cannot be simply expressed in such a simple way. Hosono's working hypothesis, which was placed outside the box, was logically derived from several experimental facts, and a few years after proposing the hypothesis, he successfully conducted and published an experiment that raised the working hypothesis to a respectable established theory. Hosono's philosophy as a scientist, in which he tries to make his "working hypothesis" not just an "idea" but an evidence-based theory, can be seen.

The author believes that the *Nature* paper published in 2004 was the result of Hosono's meticulous weaving of research results obtained in his experimental laboratories, just like weaving cloth from thread. Eighteen years after the publication of the research results, the *Nature* paper that became a source of innovation [***Nature*, 432, 488-492 (2004)**.] has become a "**Brilliant Gem of a Paper**" in the two technical fields of materials science and semiconductor electronics, marking a great step forward in the history of science and technology.

9 Acknowledgement

In this systematic survey report, the author asked Professor Hideo Hosono to confirm the scientific descriptions, especially in Chapters 3, 4, 5, and 6, only from an academic perspective. This research report contains the author's speculation, conjecture, and imagination at various points throughout all chapters. With respect to those statements, because they are the author's ideas and views as a "third party," I strongly begged Professor Hosono to refrain from commenting on them, even if they are slightly different from the facts, knowing it was very rude. The author is truly grateful for Professor Hosono's very generous response to the author's impolite request. In addition, Professor Hosono was willing to provide many of the illustrations and photographs with slight revisions to many of them that the author had requested. I would like to express my sincere gratitude to Honorary Professor Hideo Hosono for his kind understanding and response to the author's position and wishes despite his extremely busy schedule.

Because of the above background, please forgive the author if there may be some differences from the truth in what is described. In addition, due to the author's inexperience and lack of understanding of materials physics, please forgive the author if the author's description deviates from what is recognized in the academic community. The author would be happy if the readers could confirm this correctly again by reading the papers and reviews by Prof. Hosono, Prof. Kamiya, Prof. Ohta, and others.

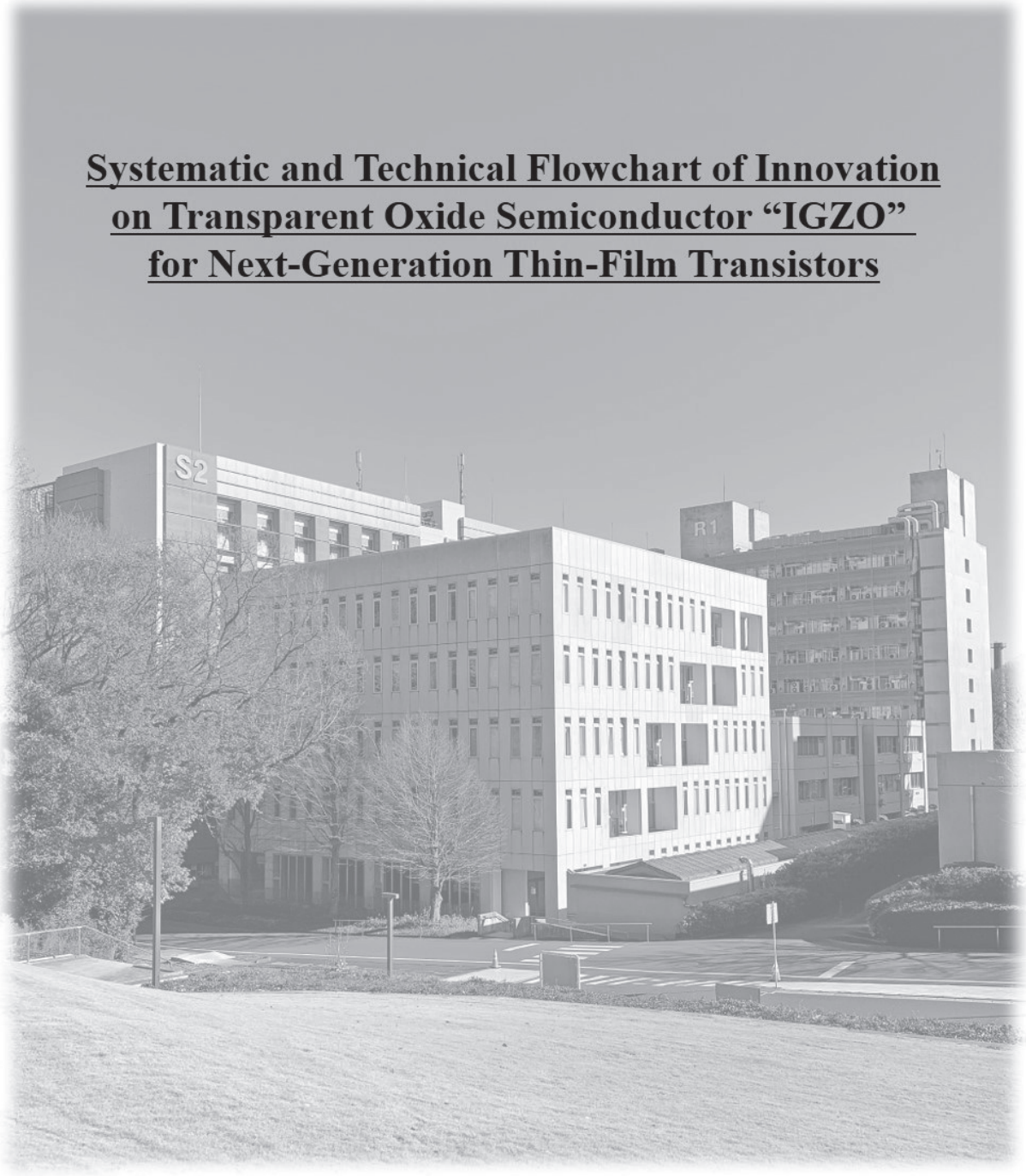
I am once again deeply grateful to Dr. Masashi Furukawa (Manager, Department of Innovation Platform, JST), who gave me an update on the ERATO "HOSONO Transparent ElectroActive Materials Project" at that time, Dr. Masaru Ozaki (then Industry-Academia Partnership Adviser, Department of Intellectual Property Management, JST), who shared with me the details of patent activities at that time, including licensing agreements in intellectual property, and Dr. Hideya Kumomi (who held concurrent posts as a Chief Specialist at the Department of Intellectual Property Management of JST, and as a Professor at the Materials Research Center for Element Strategy of the Tokyo Institute of Technology), who gave me an update on IGZO-TFTs from that time to the present, including details of patent production activities in Japan and overseas under joint research with Hosono's laboratory, thin film fabrication by sputtering, a-IGZO device development, product information, kindly provided me with materials, and during this systematic survey.

In addition, the interviews with Professor Hosono by Kenichi Takada, Yoshimitsu Goto, Masaaki Maruyama, Yoshiyuki Matsuo and Yasuhiro Yamaguchi were very informative and the author have reproduced excerpts from them in English. The author would like to express his deepest gratitude to all of them.

In addition, the following individuals extended their support in various ways during the course of this systematic survey. I want to thank: Dr. Yoshiaki Ikenoue, Dr. Yukihiro Okuno, Dr. Masahi Ono, Mr. Masaharu Kubo, Mr. Tsutomu Sasaki, Mr. Masahiro Takata, and Mr. Hideyuki Miyata. The names are listed in Japanese alphabetical order.

At the end of this systematic survey report, I have posted a photograph taken during the banquet of the "International Workshop on Elements Science and Technology for Materials Innovation", held on November 12, 2010, at Suzukake Hall on the Suzukakedai Campus of Tokyo Institute of Technology, where we met after a long time.

Fig. 9.1 A scene from the banquet of the international conference held at Suzukake Hall, Tokyo Institute of Technology in November 2010.
(Left) Prof. Hideo Hosono, (Right) The author = Masayuki Suzuki.



MDX Research Center for Element Strategy of
Tokyo Institute of Technology in the distance
(Photo by the author)

Systematic and Technical Flowchart of Innovation on Transparent Oxide Semiconductor "IGZO" for Next-Generation Thin-Film Transistors

Simple History of Transistors

■ FET J. E. Lilienfeld ■ MIS-FET O. Heil ■ Transistor J. Bardeen W. H. Brattain W. Shockley ■ MOS-FET D. Kahng M. M. Atalla ■ TFT P. K. Weimer ■ a-Si & TFT W. E. Spear Le Comber

Period: 1920s | 1930s | 1940s | 1950s | 1960s | 1970s

Major History of Oxide-TFTs

◆SnO_2-TFT (Philips): Solid State Electronics (1964).

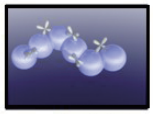
◆ZnO-TFT (Northwestern U.) Proc. IEEE (1968).

[Amorphous] ~ Amorphous $InGaZnO_4$-TFT ~

◆Physical & Chemical Properties of Amorphous/Glass Oxide Semiconductors;
① "V_2O_5-Mo_x-Glass" by E. P. Denton: Nature, 173, 1030-1032 (1954).
② "Amorphous InO_x" by J. R. Bellingham: J. Phys. Cond. Matter, 2, <28>, 6207-6221 (1990).

◆Discovery of Three Types of Amorphous Oxide Semiconductors;
① "am-$AgSbO_3$", Jpn. J. Appl. Phys., 34, <3A>, L281-L284 (1995).
② "am-2CdO·GeO_2", Appl. Phys. Lett., 67, 2663-2665 (1995).
③ "am-2CdO·PbO_x", Appl. Phys. Lett., 68, 661-663 (1996).

◆Proposal of "Hosono's Working Hypothesis";
Presentation at 16th-ICAS at Kobe, (1995).
J. Non-Cryst. Sol., 198–200, 165-169 (1996).



Courtesy of Professor Hosono

$(n-1)d^{10}ns^0$ $(n \geqq 4)$

◆Scientific Validation of the "Working Hypothesis" using Amorphous 2CdO·GeO_2 by Hosono's Pj.;
Phys. Rev. B, 66, 035203 (2002).

◆$InGaZnO_4$ Synthesis by Schmitz-DuMont;
Z. anorg. allg. Chem., 341, <5-6>, 252-268 (1965).

◆New Transparent Conductive Crystalline $InGaZnO_4$ Research by HOYA;
① Jpn. J. Appl. Phys., 34, L1550-L1552 (1995).
② Trans. Mater. Res. Soc. Japan, 20, 573-576 (1996).
③ Phys. Rev. B, 61, <3>, 1811-1816 (2000).

[Crystal] ~ Homologous System: $InGaO_3(ZnO)_m$-TFT ~

◆Discovery of Homologous Compounds by Kasper;
Z. Anorg. Allg. Chem., 349, <3-4>, 113-123 (1967).

◆TEM Observation of $In_2O_3(ZnO)_m$ by Cannard;
J. Solid State Chem., 73, <2>, 418-426 (1988).

◆Crystal Chemistry Basic Research on Homologous Oxides by Kimizuka Group;
① J. Solid State Chem., 60, <3>, 382-384 (1985).
② J. Solid State Chem., 74, <1>, 98-109 (1988).
③ J. Solid State Chem., 93, <2>, 298-315 (1991).
④ J. Solid State Chem., 116, <1>, 170-178 (1995).
⑤ J. Solid State Chem., 139, <2>, 347-355 (1998).

◆History of Oxide TFTs up to 2001;
・SnO_2-TFT (Philips): Solid State Electronics, 7, <9>, 701-702 (1964).
・ZnO-TFT (Northwestern U.): Proc. IEEE, 56, <11>, 2094-295 (1968).
・$YBa_2Cu_3O_{7-d}$-TFT (IBM Zurich): Z. Physik B, 83, 307–311 (1991).
・$(LaSr)_2CuO_4$-TFT (Mitsubishi Chemi.): Appl. Phys. Lett. 66, 1770-1772 (1995).
・SnO_2:Sb-TFT (Philips): Appl. Phys. Lett. 68, 3650-3652 (1996).
・Solution-Processed ZnO-TFT (Ohya's Gp.): Jpn. J. Appl. Phys., 40, 297-298 (2001).

◆Thermoelectric Materials Research on Homologous $In_2O_3(ZnO)_m$ by Koumoto Group;
① J. Am. Ceram. Soc., 79, <8>, 2193-2196 (1996).
② J. Jpn. Soc. Powder. Powder Metall., 44, <1>, 44-49 (1997).

◆Electrical and Optical Evaluation of Homologous Oxides by Moriga and Poeppelmeier;
① "Homologous $In_2O_3(ZnO)_m$", J. Amer. Ceram. Soc., 81, <5>, 1310-1316 (1998).
② "Homologous $InGaO_3(ZnO)_m$", J. Amer. Ceram. Soc., 82, <10>, 2705-2710 (1999).

Material Creation by Hosono and Kawazoe

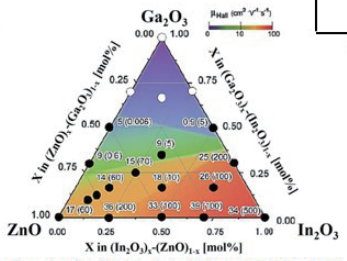
* c-$InGaO_3(ZnO)_5$ in Science (2003)
a-$InGaZnO_4$-TFT in Nature (2004)

1980s | 1990s | 2000s | 2010s

◆$YBa_2Cu_3O_{7-\delta}$-TFT (IBM Zurich:1991)
◆Sol.-Proc. ZnO-TFT (Ohya's Gp.:2001)
◆$(LaSr)_2CuO_4$-TFT (Mitsubishi Chem.:1995)
◆SnO_2:Sb-TFT (Philips:1996)

◆From Crystal $InGaO_3(ZnO)_m$ To Amorphous $InGaZnO_4$;
① MRS Symp. Proc., 623, 291-296 (2000).
② Phil. Mag. B, 81, <5>, 501-515 (2001).

◆Creation of All Amorphous Oxide p-n Junction Diode;
Adv. Mater., 15, <17>, 1409-1413 (2003).



Ref: J. Non-Cryst. Sol., 352, 851-858 (2006).

Nature,
432, 488-492 (2004).
"a-$InGaZnO_4$ TFT"

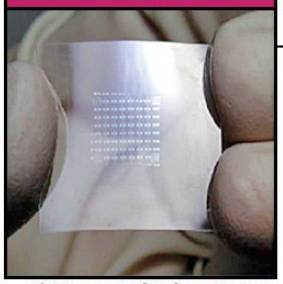


Photo courtesy of Professor Hosono

◆Presentations from 4 Groups Regarding ZnO-TFT in 2003
①Tomoji Kawai's Gp.:
J. Appl. Phys., 93, 1624 (2003).
②John F. Wager's Gp.:
Appl. Phys. Lett., 82, <5>, 733-735 (2003).
③Masashi Kawasaki's Gp.:
Jpn. J. Appl. Phys., 42, <4A>, L347-L349 (2003).
Adv. Mater., 16, <21>, 1887-1890 (2004).
④Elvira Fortunato's Gp.:
20th-ICAMS at Campos do Jordao (2003).
J. Non-Cryst. Sol., 338-340, 806-809 (2004).

Science,
300, 1269–1272 (2003).
"c-$InGaO_3(ZnO)_5$ TFT"

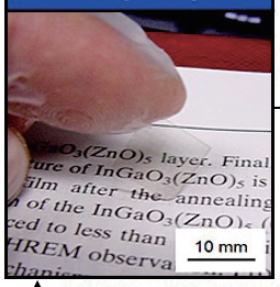


Photo courtesy of Professor Hosono

◆Selection of Optimum Carrier Concentration and Gate Insulator;
① "Growth Technique", Thin Solid Films, 411, <1>, 147-151 (2002).
② "Fabrication of MISFET", MRS Symp. Proc., 747, V2.6.1-V2.6.6 (2003).
③ "Electron Transport", Thin Solid Films, 445, <2>, 322-326 (2003).
④ "Carrier Transport", Appl. Phys. Lett., 85, 1993-1995 (2004).

◆Reactive Solid-Phase Epitaxy;
Adv. Fun. Mater., 13 <2> 139-144 (2003).
and ・J. Appl. Phys., 95, 5532–5539 (2004).
・Materials Today, 7, <6>, 42-51 (2004).
・J. Ceram. Soc. Japan, 114, <2>, 147-154 (2006).

Since the Publication of Nature (2004), Major Developments and Spreads until 2022

※The specific examples shown below are based on "IGZO-TFT" technology. This is only a small part of the development and spread of .

◆Application Development to Large Area Flat Panel Display and High-Definition Flexible OLED;
・NPG Asia Mater., 2, <1>, 15-20 (2010).
・Sci. Technol. Adv. Mater., 11, 044305 (2010).
・J Electroceram., 32, 117-140 (2014).
・Nature Electronics, 1, 428 (2018).
・SID Symp. Dig. Tech. Papers, 45, <1>, 83-86 (2014).
・Information Display, 16-21 (2016).
・ITE Trans. on Media Technol. Appl., 8, <4> 224-229 (2020).
・Information Display, 38, <5>, 60-68 (2022).

◆High Performance Stacked Active Layer System;
・"Ga-rich/Ga-poor IGZO-System" by FUJIFILM IDW2011, AMD 8-4L, 1689-1690 (2011).
・"InSnZn/InGaO-System" by Hosono's Gp. Nature Electronics, 4, 800-807 (2021).

◆P-Channel Oxide-TFT (SnO-TFT);
・Appl. Phys. Lett., 93, 032113 (2008).
・Electrochem. Solid-State Lett., 14, <1>, H13-H16 (2011).
・Adv. Mater., 23, <30>, 3431-3434 (2011).
・Adv. Mater., 28, <20>, 3831–3892 (2016).
・Nanotechnol. Rev., 8, 422-443 (2019).
・Materials, 15, 4781 (2022).

◆New In_2O_3:H-TFT;
・Nat. Commun., 13, <1>, 1078 (2022).

◆IGZO Ferroelectric-Gate FET (Memory);
・Symp. VLSI Technol. Dig. Tec. Papers, T42-T43 (2019).
・Jpn. J. Appl. Phys., 61, SC1013 (2022).

◆Application to X-Ray Flat Panel Detector;
・Med. Phys., 41, <9>, 091902 (2014).
・IEDM, 6.4.1-6.4.4(2015).
・J. Instrumentation, 12, C02045 (2017).
・Biomedical Phys. Eng. Express, 3, <4>, 045009 (2017).
・Science Advances, 4: eaat1825 (2018).
・J. Semicond., 40, 022402 (2019).
・Phys. Med. Biol., 64, <2>, 025012 (2019).
・Proc. IDW, 27, 921-924 (2020).
・npj Flexible Electronics, 4, 22 (2020).
・J. Soc. Inf. Display, 29, <5>, 390–404 (2021).
・SID Int. Symp. Digest Tech. Papers, 52, <1>, 792-794 (2021).
・Rev. Sci. Instrum., 93, 013304 (2022).
・Med. Phys., 49, <5>, 3053-3066 (2022).
・Proc. of SPIE, 11312, 113123W (2022).

◆CAAC-Technologies of SEL;
・18th AM-FPD (2011).
・SPIE–Newsroom (2012).
・ECS Trans., 54, 85-96 (2013).
・Jpn. J. Appl. Phys., 53, 04ED18 (2014).
・ECS Trans., 64, 155-164 (2014).
・Jpn. J. Appl. Phys. 53, 091102 (2014).
・Jpn. J. Appl. Phys., 55, 115504 (2016).
・Int. J. Ceramic Eng. Sci., 1, 6-20 (2019).

◆Single Crystal Growth of $InGaZnO_4$ and $(InGaO_3)m(ZnO)_n$ by Miyakawa;
・CrystEngComm, 21, 2985-2993 (2019).
・CrystEngComm, 24, 4481-4495 (2022).

◆Application to Memory by Hanyang University
・J. Alloys and Compounds, 888, 161440 (2021).
・Electronics, 11, 53 (2022).

Drawn by Masayuki Suzuki in January 2023.

Systematic Survey of Transparent Oxide Semiconductors for Thin Film Transistors Materials on the History of Industrial Technology Location Verification

Number	Name	Fabrication Year	Manufacturer	Location		Reason for Selection
1	Flexible transparent amorphous IGZO thin film transistors formed on PET	2004	• Hosono-Kamiya Laboratory, Tokyo Institute of Technology, • JST ERATO "HOSONO Transparent ElectroActive Materials Project", • JST ERATO-SORST "Function Cultivation of Transparent Oxides Utilizing Nano-Structure and Their Application"	HOSONO Office, Tokyo Institute of Technology	MDX Research Center for Element Strategy (S8 Building), Suzukakedai Campus, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Japan	Amorphous IGZO-based oxide semiconductor thin films have high operation performance as semiconductor transistors due to their wide band gap, transparency in the visible region, and high carrier controllability. Since these oxide semiconductor thin films are amorphous and can be deposited at low temperatures. This advantage has made it possible to choose organic materials such as PET as substrates. These amorphous IGZO-TFTs became a "pioneer", opening a significant door to flexible electronics. Furthermore, this technology is opening up the path to transparent electronics, and the extant material on amorphous oxide TFTs is extremely important for the industry, as a starting point for innovation. This outstanding legacy of materials science deserves to be properly preserved and passed on to future generations.
2	High-performance pulsed laser deposition (PLD) system	1997	ULVAC Co., Ltd.(Currently ULVAC, Inc)	Hosono- Kamiya-Hiramatsu Laboratory, Tokyo Institute of Technology	Room 110, R3-D Building (Creative Research Laboratory), Suzukakedai Campus,Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, JAPAN	The PLD deposition system allows control of temperature over a high-temperature range that exceeds the crystal growth temperature of oxide thin films and control of oxygen partial pressure within the chamber over a wide range. As a result, the system is a tool for creating high-performance thin film materials and exploring materials with special specifications that can be used to fabricate amorphous to epitaxial single-crystalline thin films for oxide semiconductors. This system was used in studies to publish two papers in *Science* (2003) and *Nature* (2004) journals that were outstanding achievements in materials science. In particular, amorphous IGZO-TFTs have found practical applications in numerous displays due to their advantage of film deposition at low-temperatures and have been largely deployed to various sensors and new memory devices, driving innovation. Most manufacturing equipment used by various companies today uses the sputtering method for large-area deposition during production. However, this PLD system created the starting point that paved the way for multi-component oxide thin film devices. This PLD system is extremely valuable in the history of industry and a valuable resource for both academia and industry, which is worthy of being commemorated and preserved for future generations.

＊The above two materials were registered as Essential Historical Materials for Science and Technology (MIRAI Technology Heritage) on September 10, 2024 under the following names respectively.
・Flexible and Transparent Amorphous IGZO Thin-Film Transistor
・Pulsed Laser Deposition (PLD) System for Novel Oxide Thin-Film Creation

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