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Research Center for Functional Materials: Part 2

Bringing the lab to life

Processing technologies enabling practical application of new materials

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The ultimate dream of many materials researchers is to develop materials capable of dramatically enhancing the performance and efficiency of current products, thereby enriching everyday life and solving issues vital to humankind.

However, materials development success in the laboratory does not always promise the success in real world.

Popularizing new materials requires technologies and techniques enabling their mass production at reasonably low cost while also ensuring stable quality and potential updating of the new materials.

With this in mind, researchers at the NIMS Research Center for Functional Materials (RCFM) simultaneously pursue the development of materials with novel functions and the design of practical processing technologies for them.

With the strong ambition to create truly beneficial materials, RCFM researchers strive to develop materials with the potential to transform the world in a positive way, rather than aiming for mere laboratory success.

Izumi Ichinose

Deputy Director-General and Managing Researcher
Research Center for Functional Materials (RCFM)
National Institute for Materials Science (NIMS)

Isamu Yashima

Fellow, Mitsui Mining and Smelting Co., LTD. (MMS)

Special Talk

Developing materials taking mass production into account

Processing technologies are vital to mass production of materials. Requirements and challenges for the development of processing technologies were discussed between Isamu Yashima, Fellow of Mitsui Mining and Smelting Co., LTD., who has experience in the development and mass production of various materials, and Deputy Director-General Izumi Ichinose at the NIMS Research Center for Functional Materials.

Special Talk

The experience of past failure motivated me to develop materials to be widely used in society——Isamu Yashima

New materials for better society

Ichinose: I had always thought that MMS was specialized in smelting. However, I recently found out that the company also develops various functional materials, including very thin copper foil used as wiring materials for smartphones and other electronic devices and catalysts used in automobiles and motorcycles.

Yashima: The history of MMS dates back to 1874 when the Mitsui group founded it at the Kamioka Mine in Gifu Prefecture. MMS is now operating as a full-scale raw materials manufacturer, handling a wide range of raw materials in addition to copper foil and catalysts, from battery materials to ceramics. After serving as Director of the Engineered Materials Sector R&D Center until 2015, I was appointed as Fellow and have been supporting the development of new products and technologies.

Ichinose: I understand that you have a long relationship with NIMS.

Yashima: I was a visiting researcher 30 years ago at the National Institute for Research in Inorganic Materials (NIRIM), a precursor of NIMS. I was dispatched to NIRIM from my company to study vapor-phase synthesis of diamond.

I then researched and developed thermoelectric materials capable of two-way conversion between thermal energy and electrical energy using the semiconductor techniques studied at NIMS. I then developed a material capable of generating electricity using temperature differences between body heat and the ambient environment. The material was adopted by a major watchmaker and integrated into a power generation module of watches. However, because the material was capable of generating only low levels of power barely sufficient to operate watches, its application in society was very limited. This experience motivated me to develop materials to be widely used in society.

Ichinose: When we start a project to develop new materials at NIMS, we also formulate plans to put developed materials into practical use. Although successful projects sometimes produce a number of new materials, many of them fall short of practical application in society due to various issues, such as mass production cost, quality and production yield rate.

Yashima: All manufacturers must address these issues by finding ways to produce high-quality materials at low cost. It is important for us at the MMS R&D Center to develop new materials through basic research while also developing processing technologies that will enable their mass production.

Processing technologies leveraging chemical engineering

Ichinose: What types of processing technologies have you developed?

Yashima: I have developed many processing technologies, including catalysts for automobiles. The objective of the catalysts is to continuously purify exhaust gas under the conditions in which redox states change rapidly. We have developed a catalyst material with increased capability to store and release oxygen and increased specific surface area. It was adopted for use by a major automobile maker.

When we carry out basic research on catalysts, we synthesize them using containers of several hundred milliliter capacity. However, when we mass-produce catalysts, we have to use containers of several hundred to thousand liter capacity. As the sizes of the containers increase, the chemical reactions occurring in them become increasingly uneven between the top and bottom and between the center and periphery, resulting in inconsistent catalyst quality across the container. After successful catalyst synthesis for the first trial, it has occurred that we were unable to synthesize catalysts again of satisfying quality relative to the set specifications.

Ichinose: Yes, I understand. When you synthesized the materials in small-scale experiments, both the materials and heat spread instantly across the container, but when you conducted larger-scale experiments, their movement was very limited. How did you resolve this problem?

Yashima: We first modified the reaction containers. We designed them to increase the diffusion efficiency of the reaction solutions after carefully monitoring the diffusion pathways and the pH of the reaction solutions and performing thorough computation from the perspectives of thermodynamics and solution chemistry.

In addition, the grain sizes and crystalline properties of the resulting materials vary

Catalysts for automobile exhaust gases developed by MMS. Ceramics carriers at left are for four-wheeled vehicles and metal carriers at right are for two wheels. Originally developed catalyst layer with high purification performance is coated inside the carrier.

It is crucial for us to plan methods of mass production and practical application in the early stage of materials development——Izumi Ichinose

depending on the order and rate of introducing reaction solutions into a container. Therefore, we selected reactants which were easily controllable and stable in terms of reproducing consistent results.

Ichinose: I am currently developing adsorbents used to collect flammable gases in oil fields. I found that the sizes of adsorbent containers and the amounts of gases to be collected are critical factors in this study. The adsorbents perform very efficiently in small-scale experiments in the lab, but their capability to adsorb gases at a scale comparable to real oil fields is limited. Therefore, when we develop materials and devices for large-scale use, we take approaches of gradually increasing experimental scales toward the scale of practical application.

Expediting the mass production capability through industry-academia collaboration

Ichinose: I think it is crucial for us to plan methods of mass production and practical application in the early stage of materials development and update them as we increase the experimental scales.

Yashima: I totally agree with you. It is becoming difficult, however, for companies to independently undertake the entire materials development processes from basic research to practical application amid the intensifying international competitions in materials development. An ideal approach to address this issue is to achieve collaboration between research institutions and universities—which have accumulated unique ideas on materials and processing technologies—and companies which have developed their own mass production technologies. This type of collaboration would strengthen Japan's global competitiveness in manufacturing.

Ichinose: It is also difficult for NIMS to solely develop processing technologies that will enable mass production. Thus, we are discussing our role in mediating collaboration between research institutions and the industrial sector.

The RCFM at NIMS launched a project to develop processing technologies to identify precursors to functional materials in 2016. We hope to bring innovation in collaboration with the industrial sector by formulating materials development plans taking processing technologies into account. Superconducting wires featured in this NIMS NOW issue (see p. 6) are the type of materials we are focusing on in this project. We are also developing processing technologies for various other materials, such as next-generation semiconductor materials (see p. 8) and high-performance ceramics (see p. 10).

Yashima: Development of mass production technologies requires the use of basic scientific data. Appropriate data being available to companies greatly facilitates their efforts to develop such technologies. I hope that NIMS can provide reliable data to us so that we can work together to mass-produce and popularize novel materials.

Unlimited potential of processing technologies

Ichinose: Processing technologies sometimes enable identification of completely groundbreaking properties in materials that appear to have been fully studied. For example, rapid cooling of melted metals produces high-strength metallic glasses. In addition to reexamining existing materials, we are also committed to developing processing technologies enabling the creation of novel materials which was impossible using the current technology.

Yashima: Invention of world's-first, groundbreaking products today requires flexible thinking and ideas from various angles. I have high expectations for NIMS to deliver even more innovative materials and processing technologies than ever before.

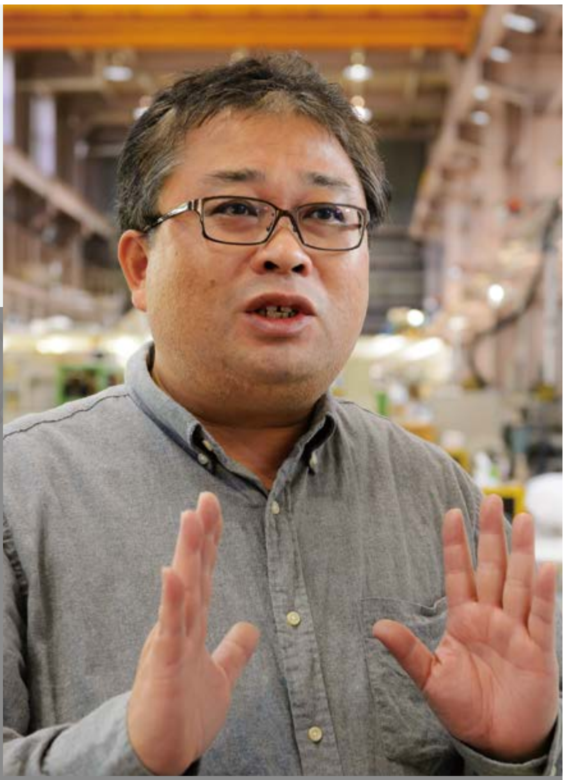
(by Shino Suzuki, PhotonCreate)

Process 1

Processing technique to produce high-performance superconductors

Perfecting the fabrication of superconducting wires

Superconducting magnets—capable of producing powerful magnetic fields without generating electrical resistance and heat—have been used in various technologies. However, fabrication of superconducting magnets requires the processing of superconducting materials into wires, and it is not easy. Akihiro Kikuchi has been pursuing the development of new processing techniques at NIMS, an organization leading the world in wire fabrication technologies.



Akihiro Kikuchi
Leader,
Low-Temperature Superconducting Wire Group,
Research Center for Functional Materials

Bronze process invented by NIMS

Superconducting magnets have been used in various technologies, such as medical MRI (magnetic resonance imaging), NMR (nuclear magnetic resonance spectroscopy), magnetic levitation trains, particle accelerators and nuclear fusion reactors. More than 90% of these superconducting magnets are composed of niobium titanium (NbTi) superconducting alloys. NbTi has an issue, however: its critical magnetic field is approximately 10 tesla, beyond which its superconductivity ceases. More powerful magnetic fields would enable increased NMR resolution and the use of higher energy levels in particle accelerators. For these purposes, triniobium tin (Nb_3Sn) has attracted a great deal of attention due to a critical magnetic field strength more than twice that of NbTi. NIMS and its predecessor organization (the National Research Institute for Metals) have led the world in the development of Nb_3Sn wires. Akihiro Kikuchi of the Low-Temperature Superconducting Wire Group has assumed responsibility for developing processing techniques to further improve Nb_3Sn wire performance.

“NbTi is widely used today as a wire material because it can be processed into wires of various shapes using versatile techniques,” said Kikuchi. “On the other hand, Nb_3Sn is hard and brittle and difficult to process into wires. Research and development efforts have been underway worldwide to find ways of fabricating Nb_3Sn wires. NIMS has developed a wire fabrication technique called a ‘bronze process’.”

In the bronze process, several holes are created along the length of a cylinder composed of bronze—an alloy of copper and tin (Sn). Niobium (Nb) is inserted into the holes and the alloy is stretched into a thin, long piece in a manner similar to a kintaroame (a type of cylindrical Japanese candy whose cross-sectional decorative patterns are identical along its entire length). The process is repeated to produce hundreds of these elongated materials, which are then bundled together and further stretched into a fine wire. This procedure enables fabrication of a wire with a consistent cross-sectional bronze-Nb arrangement along its length at room temperature. Finally, the wire is thermally treated to convert its Nb multicore—each core being a few microns in diameter— into an Nb_3Sn multicore. Bronze-processed Nb_3Sn superconducting wires have been used in the ITER (International Thermonuclear Experimental Reactor) project in France.

“Even if a very effective technique is developed, if its application is limited to small-scale production, it will only be useful for publication in research papers,” Kikuchi said. “It is important for processing techniques to be compatible with the subsequent wire elongation step in order for them to be practical in the real world.”

Enhancing the performance of bronze-processed Nb_3Sn wires

To further increase the critical current density of Nb_3Sn wires—which are already in practical use—their Nb_3Sn content

Figure 1. (Top) Structurally controlled bronze material containing a high concentration of Sn (18.5% by mass). It elongates by 200% at 600°C. (Bottom) Conventional, structurally uncontrolled bronze material.

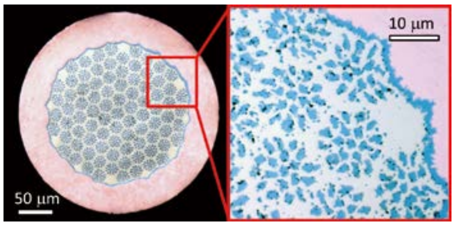


Figure 2. Newly developed bronze-processed, ultrafine, multicore Nb_3Sn superconducting wire containing the world's highest concentration of Sn. Its outer diameter is 0.3 mm. A total of 1,615 superconducting filaments are enclosed internally, with each filament a few microns in

needs to be increased by using bronze with higher Sn content.

NIMS fabricates bronze-processed Nb_3Sn wires using bronze produced by Osaka Alloying Works, Co., Ltd. in Fukui Prefecture. To be appropriate for use as a raw material in the production of superconducting wires, bronze needs to be homogeneous in microstructure and composition. Osaka Alloying Works has the skill necessary to achieve this. The maximum possible Sn content of bronze had been 16% by mass, beyond which it became susceptible to breakage and could not be processed into wires. To address this issue, Kikuchi and Osaka Alloying Works jointly pursued ways of increasing the Sn content of bronze.

"We found that titanium (Ti), a bronze additive, was the key," Kikuchi said. "Formation of a solid solution composed of Nb_3Sn and Ti had been known to increase the critical current density of Nb_3Sn wires under a strong magnetic field. That is why a trace amount of Ti is added to bronze. Our detailed study on the behavior of Ti in bronze revealed that Ti selectively binds to Sn in bronze to produce a stable Cu-Sn-Ti compound."

"We added an increased amount of Ti, in addition to an increased amount of Sn, to bronze, which led to the world's highest Sn content of 18.5% by mass. Furthermore, we succeeded in increasing the ability of bronze to elongate by finely and uniformly distributing Cu-Sn-Ti compounds throughout the microstructure of bronze (Figure 1)."

In 2016, Kikuchi finally succeeded in fabricating ultrafine Nb_3Sn multicore wires using the newly developed bronze (Figure 2).

Fabrication of Nb_3Al wires using techniques suitable for industrial use

Kikuchi is currently undertaking the challenge of putting triniobium aluminum (Nb_3Al) into practical use as a third-generation superconducting material.

"The superconductivity of Nb_3Al is more resistant to strong magnetic fields than that of Nb_3Sn. Nb_3Al is also less susceptible to bending and tensile strain," Kikuchi said. "Because Nb_3Al possesses these two characteristics ideal for high-field electromagnets, many researchers are anxiously awaiting its practical application."

However, unlike Nb_3Sn, Nb_3Al cannot be produced using the bronze process. NIMS, therefore, is pursuing the production of Nb_3Al wires using a "jelly roll process" and a "rapid heating and quenching process."

"The first step in the jelly roll process is to roll thin sheets of Nb and aluminum (Al) together. The jelly roll process was so named because the cross-section of the rolled material resembles that of a jelly roll (Figure 3). The rolls are then stretched to form hexagonal bars, and a bundle of several hundred bars is processed into a multicore wire. This process fills gaps between the Nb and Al sheets to several nanometers, thereby facilitating the reactions between them which form Nb_3Al. The wires are then thermally treated. While Nb_3Sn wires are normally exposed to 700-800°C temperatures, Nb_3Al wires need to be exposed to much higher temperatures of approximately 2,000°C, at which they reach a stable phase and form a desirable crystalline structure. To achieve this thermal treatment, NIMS developed a rapid heating and quenching process whereby wires are placed in a high-vacuum chamber and heated to 2,000°C by alternately wrapping them around one of two drums, enabling direct current to pass through them. Heated wires are then allowed to cool rapidly in a liquid gallium (Ga) bath, which is at approximately room temperature (Figure 4). This technique enabled Nb_3Al wires to elongate.

A major issue remains to be overcome before the above-mentioned techniques can be practically applied. "I think that the jelly roll process and the rapid heating and quenching process are the right combination for the production of Nb_3Al wires," Kikuchi said. "However, for these processing techniques to be widely adopted, further research is necessary to improve their compatibility with companies' existing technological infrastructures. In addition, demand is high for further enhancement of wire performance."

NIMS recently acquired the capability to produce jelly roll-processed wires at its facility. This acquisition made NIMS the world's lone research organization with the capability to perform two unique techniques—the jelly roll process and the rapid heating and quenching process. Thus, NIMS is now capable of producing Nb_3Al wires approximately one kilometer in length at its facility for use in R&D activities. "I hope that researchers and engineers in Japan and other countries will visit NIMS to learn about the processes we have developed. I would really like to promote practical application of these techniques by disseminating them around the world," said Kikuchi enthusiastically.

(by Kumi Yamada)

H. Taniguchi et al. 2015. TEION KOGAKU. 50: 186-193.
A. Kikuchi. 2018. TEION KOGAKU. 53: 27-34.

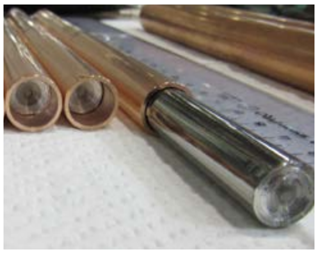


Figure 3. Jelly roll-processed billets fabricated at the NIMS facility. The billets are produced by wrapping Nb and Al foil of 0.1 mm and 0.03 mm in thickness, respectively, around a Nb core bar. To produce a multicore wire, a billet is processed into a thin wire by inserting it into a copper tube and pushing it out using a hydrostatic extrusion process. Hundreds of thin wires are then bundled together to form a multicore wire.

Figure 4. Rapid heating and quenching system developed by NIMS. At lower right is the heart of the system (detailed photo in the lower portion of the cover). A material to be processed is first heated until its temperature rises to approximately 2,000°C by passing direct current through it in a chamber between a pure copper pulley and a liquid gallium (Ga) bath. The material is then rapidly cooled in the Ga bath. This process enables fabrication of materials with desirable high-temperature phase properties at room temperature.

Process 2

Hottest new material for next-generation semiconductor

Perfecting the synthesis of α-gallium oxide (α-Ga_2O_3) films.

Great efforts are being made to develop high power conversion efficiency semiconductor materials capable of withstanding high voltages and high temperatures for power control devices. Gallium oxide (Ga_2O_3) is a rapidly emerging next-generation power semiconductor material which is expected to be put into practical use in the near future. Yuichi Oshima is researching and developing a technology to synthesize so-called α-Ga_2O_3 crystals.

Yuichi Oshima
Senior Researcher,
Optical Single Crystals Group,
Research Center for Functional Materials

Ga_2O_3—a potentially superior semiconductor to SiC and GaN

Power control devices, such as converters, perform AC/DC conversion, voltage conversion and other functions. They are incorporated into various electrical devices, including industrial devices and home appliances. Demand for the development of power control devices capable of withstanding higher voltages and higher temperatures has been growing in recent years to further increase the energy efficiency of vehicles, server computers, etc. Efforts have been made to increase the energy efficiency of power control devices by developing "novel power semiconductor materials" as alternatives to conventionally used silicon materials. For example, silicon carbide (SiC) has been put into practical use in 2014 and gallium nitride (GaN) is currently under development. In addition, expectations for gallium oxide (Ga_2O_3) are rising rapidly due to its wider bandgap, which may enable it to withstand higher voltages and be more energy efficient. Yuichi Oshima of the Optical Single Crystals Group has been researching and developing the α phase of Ga_2O_3.

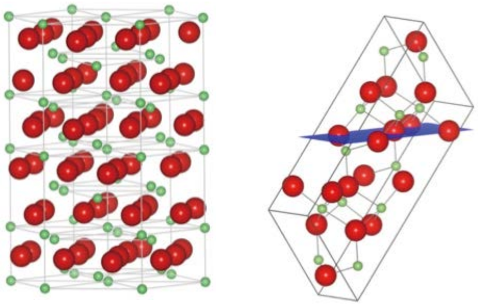
"Ga_2O_3 can be classified into different polymorphs, such as α and β, based on its crystalline structure," said Oshima. "The bandgaps—a critical property of power semiconductor property—of β and α-Ga_2O_3 crystals are 4.5 eV and 5.3 eV, respectively, which are much higher than those of SiC and GaN crystals, which are 3.5 eV or less. These bandgap comparisons indicate that Ga_2O_3 has great potential to serve as a superb power semiconductor. R&D activities in the past mainly focused on β-Ga_2O_3 rather than α-Ga_2O_3 due to some issues with the substrates."

Challenges in developing high-quality substrates

To fabricate power semiconductor devices, high-quality single-crystal semiconductor films first need to be synthesized. Such films can be grown epitaxially only on crystalline substrates with the crystal structure and lattice constants similar to those of the films being synthesized.

The preparation of appropriate substrates, however, poses some problems, as mentioned above. High-quality, single-crystal β-Ga_2O_3 films can be homoexpitaxially grown on high-quality melt-grown crystalline substrates. On the other hand, α-Ga_2O_3 is a meta-stable material, making its melt growth impossible in principle. The type of crystalline substrate which enables α-Ga_2O_3 crystals to be grown had been difficult to

Figure 1. Comparison between α-Ga_2O_3 and β-Ga_2O_3



α-Ga_2O_3
(corundum structure)

β-Ga_2O_3
(β-gallia structure)

synthesize. In addition, because the crystal structure and lattice constants of α and β-Ga_2O_3 crystals differ, the crystalline substrates required to grow β-Ga_2O_3 crystals are incompatible with epitaxial growth of high-quality α-Ga_2O_3 crystals (Figure 1).

"I thought that the outstanding properties of the α-Ga_2O_3 material really should be exploited even though proper substrates enabling their growth were unavailable at the time," said Oshima. "I then came up with the idea of using the halide vapor phase epitaxy (HVPE) method to overcome this issue. I hoped to expedite the development of α-Ga_2O_3 power semiconductors by applying the HVPE technique to the synthesis of crystalline substrates on which α-Ga_2O_3 crystals can grow."

Leveraging experience in developing GaN substrates to produce high-quality Ga_2O_3 substrates

During the implementation of the HVPE method—a chemical vapor deposition (CVD) method—chloride gases are produced which react on a crystalline substrate surface, inducing deposition of semiconductor crystals on the substrate (Figure 2). Other epitaxial growth techniques are available, such as metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). But the rate of crystal deposition using the HVPE method is 100 to 1,000 times greater than that of the MBE method, the most widely adopted method in R&D related to Ga_2O_3 power semiconductors.

"The capability of the HVPE method to speedily deposit single-crystal semiconductor films may reduce film production cost, given that thick films are required to increase the breakdown voltage of power devices," said Oshima.

"In addition, α-Ga_2O_3 crystals can grow epitaxially on a crystalline sapphire substrate as both α-Ga_2O_3 and the substrate have the corundum structure. Another problem exists, however: a difference in lattice constants between sapphire and α-Ga_2O_3 causes crystalline defects to develop in α-Ga_2O_3 crystals as they grow. Crystals are often required to grow into thicker layers to a certain degree to reduce the number of defects. Because the HVPE method enables high-speed deposition of crystals, it is superior to other epitaxial growth techniques in synthesizing high-quality crystals."

"For many years before coming to NIMS, I worked on the synthesis of GaN crystals using the HVPE method. Like other types of crystals, GaN crystals had the problem of crystalline defects due to the difference in the lattice constant between GaN and its substrate. We eventually succeeded in mass-producing high-quality substrates by taking creative approaches, such as applying a selective area growth technique and a technique to reduce stress on crystals by forming voids at the growth interface. I am currently leveraging that experience to develop high-quality Ga_2O_3 substrates."

Oshima already succeeded in synthesizing world's first α-Ga_2O_3 films using the HVPE method in 2014 (Figure 3).

Combining film deposition methods to develop practical processing techniques

Successful growth of α-Ga_2O_3 films was achieved using a mist CVD method before it could be achieved using the HVPE method. Kyoto University Professor Shizuo Fujita is the leading authority on this methodology. In the mist CVD method, an aqueous solution of constituent elements is vaporized into mist and introduced into a crystal growing furnace, allowing semiconductor crystals to be deposited on a substrate.

"Adoption of the mist CVD method for this purpose has some advantages. The technique can be performed safely and at low cost because it does not require the use of toxic or flammable gases or a system equipped with a vacuum pump. In addition, the technique enables a crystal to grow into a multilayered film with precision," said Oshima. "However, like other epitaxial growth techniques, the high density of crystal defects, which is attributed to the use of sapphire substrates, is still a major problem.."

"To address this problem, I proposed the development of a processing technique which would exploit the strong points of both the HVPE and mist CVD methods. My vision is to create a high-quality substrate using the HVPE method and then grow a crystalline device structure on the substrate using the mist CVD method. To put this idea into practice, I am currently working to further improve the quality of α-Ga_2O_3 crystals grown using the HVPE method."

Oshima, Professor Fujita, FLOSFIA (a venture firm under the aegis of Kyoto University) and Saga University have been working together on a joint research project sponsored by NEDO (New Energy and Industrial Technology Development Organization) since FY2017.

"I would like to achieve further miniaturization, weight reduction and increased energy efficiency in electrical devices and automobiles, thereby promoting a low carbon society," said Oshima. "The R&D related to both α and β-Ga_2O_3 began only recently. I hope to establish practical processing techniques to produce them in the near future."

(by Kumi Yamada)

Y. Oshima et al., Appl. Phys. Express 8, 055501 (2015)

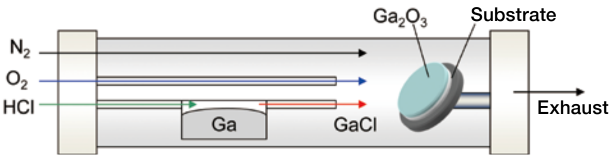


Figure 2. Schematic diagram illustrating the halide vapor phase epitaxy (HVPE) method
The reaction of Ga with HCl forms GaCl, which in turn reacts with O_2 gas to form Ga_2O_3.

Figure 3. α-Ga_2O_3 film synthesized using the HVPE method


Oshima succeeded in growing single-crystal films of approximately 2 inches in diameter.

SEM cross-section image

Process 3

Improving transparency and processability with low temperature

Perfecting the fabricating process of highly-functional ceramics

Ceramics exhibit superior resistance to heat and corrosion. Sintering and plastic deformation of ceramics are normally performed at temperatures above 1,400°C. To enhance current sintering methods, Byung-Nam Kim and Hidehiro Yoshida of the Field-Assisted Sintering Group, NIMS, have been studying ceramic fabrication techniques applicable at temperatures below 1,000°C.

Hidehiro Yoshida

Principal Researcher,
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Byung-Nam Kim

Leader,
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Research Center for Functional Materials

Investigating sintering mechanisms

Ceramics are produced by sintering powdered oxides, nitrides or other compounds at high temperatures. Because ceramics are very hard and more resistant to heat and corrosion than metal materials, they have been used in various systems, such as automobile engine parts and information and communications devices.

Sintering ceramics, however, requires large amounts of energy and is costly due to the need to use temperatures above 1,400°C. In addition, because ceramics are difficult to deform into complex shapes by applying force, the range of their practical applications is limited.

"Our goal is to develop ceramic processing techniques applicable at temperatures below 1,000°C—which will enable production of ceramics with novel properties and functions—by understanding sintering mechanisms through theoretical, experimental and computational approaches," said Kim and Yoshida.

Developing optimum techniques for creating hard, transparent ceramics at lower temperatures

Two lower-temperature sintering methods had been studied in the past, involving the application of pressure and electric fields. When pressure is applied to ceramic compound powders, they densify, lowering their sintering temperatures. Application of electric fields can also lower sintering temperatures as it allows direct heating of ceramic compounds, rather than in a furnace.

"However, many factors need to be considered before these approaches can be pursued," said Kim. "Numerous combinations of pressure levels, electric field strengths and durations and methods of applying them exist. Changing these parameters greatly affects the properties of sintered ceramics."

Kim and Yoshida have spent many years developing transparent ceramics made from oxides, such as aluminum oxide (Al_2O_3) and yttrium oxide (Y_2O_3).

"Transparent ceramics are potentially applicable in white light-emitting diodes (LEDs), for example. The phosphor powders currently used to emit white light are solidified by mixing them with resin. If elements that function as phosphors could be mixed with Al_2O_3 or Y_2O_3, and then sintered into transparent ceramics, resin would be unnecessary. Because ceramics are harder and more heat resistant than resin, incorporating ceramics may extend the lives of LED products."

The production of transparent ceramics requires refinement of ceramic compound particles to approximately 100 nanometers, completely eliminating gaps between them. However, if these particles are sintered at temperatures as high as 1,400°C, reactions occur between adjacent particles, inducing them to grow and generating gaps between them. On the other hand, sintering at lower temperatures prevents particles from growing, resulting in the production of hard and transparent ceramics.

Yoshida performed repeated experiments in which he sintered refined oxide powders while applying various combinations of pressure and electric fields. In 2016, he discovered that with pressure under 170 MPa (megapascals), they can create transparent ceramics by sintering Y_2O_3 powders at temperatures below 1,000°C (Figure 1). The technique Yoshida developed achieved three successes at once: highly transparent and hard ceramics and energy-efficient sintering.

"The highest transparency can be achieved at 170 MPa—no more and no less—although we have little understanding of why," said Kim. "We are currently analyzing the relationship between particle size, temperature, pressure, electric fields and ceramic properties through computation and microscopic observation. We hope that our efforts will lead to the development of theoretical sintering models applicable to various types of materials in the near future."

Creating expandable ceramics by applying electric fields

"Additional advantages of applying electric fields to sintering—other than the ability to directly heat ceramic compounds—have been identified recently, after the discovery of the so-called "flash sintering" phenomenon in the United States in 2010," said Yoshida.

Flash sintering occurs when the following procedure is used. First, Y_2O_3 powder—a type of oxide more resistant to electric fields than Al_2O_3, another oxide—is solidified by applying pressure. Electrodes are then directly attached to the solidified Y_2O_3 powder and an electric field is applied. If voltages lower than 300 V/cm are applied, the particles gradually densify as their temperatures increase to 1,400°C. By contrast, if voltages higher than 500 V/cm are applied, particles rapidly densify in about 10 seconds at a certain point during sintering. Y_2O_3 densified at 1,100°C when a voltage of 500 V/cm was applied and at 1,000°C when a voltage of 750 V/cm was applied—lower than the conventional sintering temperature of 1,400°C. Many researchers—myself included—were inspired by the discovery of flash sintering and began investigating its mechanisms. The most widely accepted current theory is that flash sintering occurs when particles undergo rapid self-diffusion—fast movement of atoms within a material under the influence of electric fields. When flash sintering occurs, self-diffusion accelerates by approximately 1,000 times." Yoshida continued.

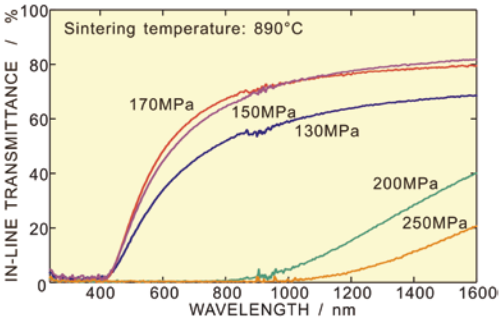


Figure 1.

An electric field of approximately 10 V/cm was applied to Y_2O_3 powder being sintered under various pressures. The resulting sintered ceramic samples are shown at upper left. The study found that high density and highest degree of transparency are achieved in ceramics sintered at temperatures below 1,000°C under a pressure of 170 MPa.

"An interesting idea came to me one day. While a ceramic material is undergoing rapid self-diffusion, perhaps it would be possible to deform it easily by applying stress."

To put this idea into practice, Yoshida attempted to deform densified zirconium oxide (ZrO_2), a high-strength ceramic material, by applying an electric field. In 2016, he succeeded in elongating the material by approximately 2.5 times its original length at the low temperature of approximately 800°C under pressures below 15 MPa (Figure 2).

Yoshida explained that this plastic deformation is enabled by a phenomenon called "grain boundary sliding" (Figure 3). Grain boundary sliding normally occurs only at temperatures above 1,400°C. However, when atoms are undergoing rapid self-diffusion as described above, they are thought to be more susceptible to grain boundary sliding. Yoshida is currently investigating the link between these two phenomena.

"We found that the technique we developed requires less energy and is capable of expediting plastic deformation of ceramics by more than 10 times compared to conventional methods. In the future, the technique may be applicable to the casting of automobile engine parts at temperatures below 1,000°C—a range comparable to plastic deformation of metals—at low cost. We will continue to study sintering mechanisms in order to identify optimum sintering conditions for ceramics. We will also strive to discover ceramics with novel properties and functions," said Kim and Yoshida with renewed determination.

(by Kumi Yamada)

B.-N. Kim et al., Scripta Mater.57, 607 (2007) DOI: 10.1016/j.scriptamat.2007.06.009
H. Yoshida et al., Scripta Mater. 146, 173 (2018) DOI: 10.1016/j.scriptamat.2017.11.042
H. Yoshida et al., J. Eur. Ceram. Soc., (2018) in press.

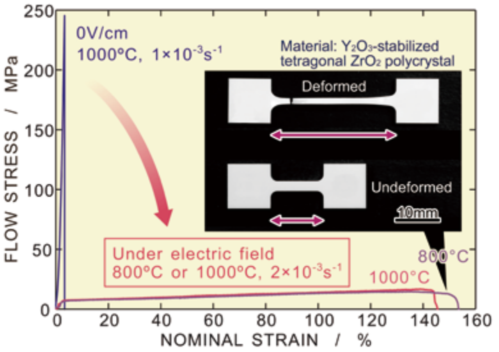


Figure 2.
High-speed, low-temperature ceramic processing using electric fields

Ceramics sintered at 1,000°C without being exposed to an electric field broke easily under stress (blue line). By contrast, ceramics sintered at a lower temperature of 800°C under the influence of an electric field underwent gradual deformation when low stress was applied, achieving elongation of up to 150% (purple line).

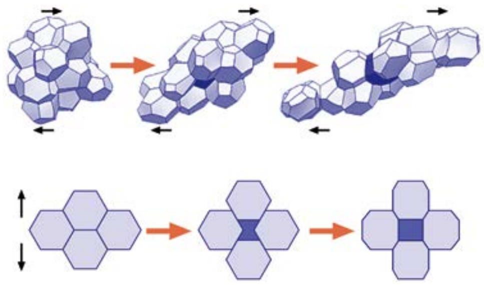


Figure 3.
Grain boundary sliding in deforming ceramics

Top: From "F. Wakai et al. 2002. Acta Materialia. 50: 1177."
Bottom: From "K. Hiraga. 2007. Journal of the Ceramic Society of Japan. 115: 395."

Deformation of a polycrystalline material occurs when tiny grains change their relative positions while retaining the bonds between them.

Physical mechanism investigation

Vol.❷

Electrically conductive organic materials

Designing organic conductors containing protonic defects that conduct electricity like metals

In search for novel materials, it is vital to understand their fundamental physical mechanisms. Continuing from the last NIMS NOW issue, in this Research Center for Functional Materials issue part 2, we will feature basic research developments with the potential to lead the discovery of innovative materials: newly discovered electrical conduction mechanisms in organic materials potentially applicable in electronic devices.

Yuka Kobayashi
Principal Researcher,
Molecular Design and Function Group,
Research Center for Functional Materials

Rising demand for electrically conductive organic materials

Organic conductors are drawing attention as key materials for the development of bendable displays and wearable devices.

Unlike conventional inorganic electronic materials, such as silicon and metals, organic materials are light and processable. For example, organic conductors can be deposited like inks onto thin, flexible sheets.

Organic materials are inherently incapable of conducting electricity. This common assumption, however, was first challenged when charge-transfer complexes were discovered in the 1950s. Professor Hideki Shirakawa then earned a Nobel Prize in 2000 for creating conductive polymers. Yuka Kobayashi at NIMS is attempting to develop even better “third-generation organic conductors.” What kinds of materials is Kobayashi seeking to create?

Dilemma of organic conductors

Although it is anticipated that conductive polymers will be used in touch panels of ATM (automated teller machine) and in battery electrodes, their actual application currently remains limited. As Kobayashi explained, “Conductive polymers have some concerns in chemical stability and durability issues, limiting their practical application.”

For materials to be electrically conductive, they must be capable of generating charge carriers. Charge carriers include negatively charged electrons, positively charged holes (vacant electronic states) or protons. Organic materials inherently do not generate carriers as they stably hold electrons and holes within their molecular structures. However, conductive polymers which are composed of conjugated molecules with a dopant—are capable of generating carriers.

“When materials are composed of combinations of electronically different types of molecules, namely doping using a dopant molecule, the bonds between the molecules and molecular structures are prone to breakage,” said Kobayashi. “It is desirable for molecules to be structurally stable and unbreakable. At the same time, electrical conductivity requires the combination of two different types of molecules. To resolve this contradiction, I considered the approach of creating organic materials that are both stable and conductive.”

Designing novel organic conductors at the quantum level

Kobayashi first designed an organic molecule to be used in creating a pure organic conductor. “My specialty early in my carrier was quantum chemistry. Using this expertise, I meticulously designed organic molecules capable of generating charge carriers, taking into account such details as atomic orbitals. I am indeed a molecular designer.”

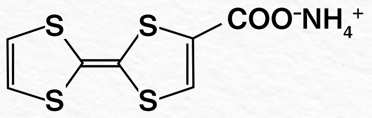
Kobayashi decided to focus on an organic molecule called tetrathiafulvalene (TTF). “TTF contains sulfur atoms. The atomic orbitals of sulfur atoms include 3p orbitals which extend farther out from the nucleus. I thought that TTF, with its extended molecular orbitals, would be conducive to high electrical conductivity if we could induce charge injection in it well, although TTF is normally insulating in itself without existence of acceptor molecules” said Kobayashi.

Kobayashi was unable to produce the kinds of results she had hoped to, however. Despite a great deal of time-consuming trial and error, Kobayashi and graduate students in her lab could not produce the desired results. “We worked through the adversity with a single conviction: if we were able to form an orderly arrangement of TTF molecules capable of generating very strong charges and high electron mobility, we would be able to create molecules with the desired properties,” Kobayashi recalled.

In 2009, several years after the research project began, Kobayashi and her colleagues finally succeeded in designing a molecule by combining TTF, carboxylic acids and ammonia (Figure 1). This molecule exhibited electrical conductivity even in powdered crystalline form.

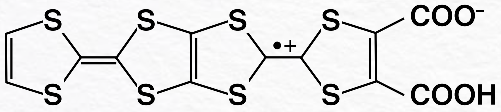
What caused the pure organic material to be electrically conductive? Combining TTF with carboxylic acids and ammonia led to the formation of a molecular network held together by hydrogen bonds. Detailed examination revealed that some of the hydrogen

Figure 1. Structures of pure organic conductors



TTF

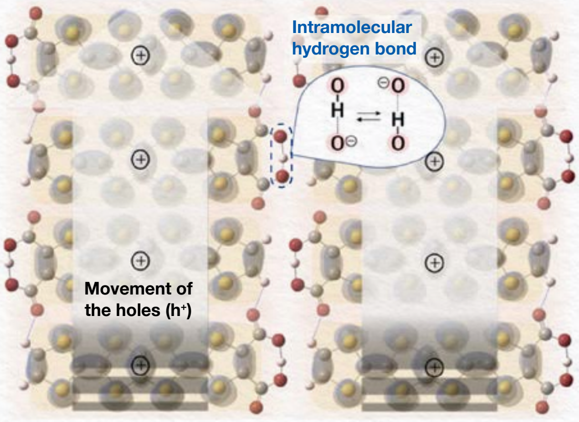
Tetrathiafulvalene (TTF) is composed of two pentagonal structures. Kobayashi added a carboxylic acid (COOH) and ammonia (NH_3) to TTF in her molecular design.



TED

TED—consisting of two TTF molecules bound together—achieved a conductivity of 530 S/cm, a value comparable to conductivities of metals.

Figure 2. Conceptual diagram of a molecular arrangement in a pure organic conductor, TED, showing the movement of protons (H^+) and holes (h^+) caused by protonic defects.



The diagram shows holes moving through TED molecules. The molecular arrangement above prevents localization of positive charges, enabling uniform distribution of electric fields across the molecules. This phenomenon is consistent with the observation that application of even a weak electric field can trigger the movement of holes. Confining protonic defects within hydrogen bonds enables holes to move freely between molecules.

bonds in the network lacked hydrogen ions (protons). “The partial absence of positively charged protons drives the generation of radical cations (electrons) which compensate the positive charges of missing protons. This shift subsequently creates holes which carry electricity as they move,” Kobayashi explained. This revolutionary organic molecule has been called a protonic-defect induced organic conductor—considered to be a “third-generation organic conductor,” following the invention of charge-transfer complexes and conductive polymers.

Achieving electrical conductivity comparable to that of metals

The electrical conductivity of the organic conductor Kobayashi developed in 2009 was 10^{-4} S/cm at room temperature. The “S” (a symbol for “siemens”) is a unit of electrical conductance, expressed as a reciprocal of electrical resistance. The measurement indicated that the organic material was electrically conductive, but only barely. Thus, Kobayashi continued to design molecules with higher conductivities, eventually leading to the development of an organic conductor in 2016 with the conductivity of 530 S/cm—a value comparable to the conductivities of metals.

How was Kobayashi able to increase electrical conductivity by more than a million times? “That is the art of molecular design,” said Kobayashi. She connected two TTF molecules and two carboxylic acids to create TTF-extended dicarboxylate (TED) (Figure 1). The use of TED with extended molecular orbitals increased the electrical conductivity of the material by ten thousand times. In addition, molecules were designed in such a way that they confined their hydrogen bonds within themselves, increasing the electrical conductivity of the material to a great extent. The increased conductivity was achieved by confining protons within intramolecular hydrogen bonds, which allowed holes to move freely without being slowed by dragging “heavy” protons. In other words, the confined protons are no longer able to trail and slow traveling holes, increasing the mobility of the holes (Figure 2).

Other studies have also reported similar levels of electrical conductivity in pure organic materials composed of radical molecular conductors. However, all of these records were made under extremely high pressures of 1 gigapascal or higher. TED is distinctive in that its electrical conductivity is as high as metals even under ambient pressure. “There are possibilities that conductivity of TED can be increased by another 10 times. I am currently working on it,” said Kobayashi.

Being a pure organic material, TED is stable, durable and easy to be synthesized. In addition, TED is soluble in organic solvents, rendering it printable on various substrates.

Other physical properties of TED

Kobayashi has been carrying out research at University of Oxford in the UK since June 2017 through a NIMS exchange program. “Metals can be characterized by various physical properties in addition to electrical conductivity,” said Kobayashi. “The material we developed also exhibits interesting physical properties. For example, it is also sensitive to external stimuli, such as heat and magnetic fields. To exploit these properties, I am conducting joint research with a researcher with expertise in device development. I cannot yet disclose the specific applications we are pursuing. For now, I can only comment that this organic conductor has great potential applicability due to the novel techniques used to produce it. I look forward to publishing our research results in the near future.”

(by Shino Suzuki, PhotonCreate)


photo: Nacása & Partners Inc.

Solution of pure organic conductors

THE RESEARCH COLUMN

Evaluation techniques that optimize the processing of materials

Secondary ion mass spectrometer (SIMS)

Techniques that can be used to characterize defects and impurities in materials are indispensable to the development of high-quality materials and processing methods. This article demonstrates the actual application of a secondary ion mass spectrometer (SIMS) capable of analyzing a wide range of materials, including metals, ceramics and semiconductors.

Isao Sakaguchi
Leader, Ceramics Surface and Interface Group,
Research Center for Functional Materials

Key role of impurities in materials development

Defects and impurities are important elements in characterizing materials under development. They may either degrade the performance of materials or add desirable functions to them in controlled amounts. Defect and impurity evaluation techniques are vital in assessing both their positive and negative effects on materials. Evaluation results are used to improve the quality of materials being developed by making modifications to raw material choices and materials processing.

The SIMS—one of the analyzers Isao Sakaguchi uses—irradiates the surface of a solid sample material with an ion beam, causing the material to eject some atoms and generating secondary ions. A SIMS discriminates the secondary ions by mass and quantifies them (Figure 1). “A SIMS is capable of detecting all of the elements found in sample materials,” said Sakaguchi. “It has ppm-level detection sensitivity; that is, it can detect one atom of an impurity out of one million atoms.”

A SIMS can analyze a diverse array of materials, including metals, ceramics, semiconductors and even biological materials. Sakaguchi’s research is currently focused on ceramics.

Analyzing oxygen defects

The electrical resistance of oxide semiconductors (i.e., ceramics)—such as zinc oxide (ZnO) and tin oxide (SnO_2)—changes when they are exposed to gases. This property makes ceramics promising gas detection materials. “The sensitivity and selectivity of ceramics to gases changes greatly depending on the types and amounts of defects and impurities,” said Sakaguchi. “Oxygen defects—the absence of oxygen atoms from lattice positions where they are normally present—play a particularly important role in determining the properties of materials. Isotope analysis using a SIMS enables us to characterize oxygen defects.”

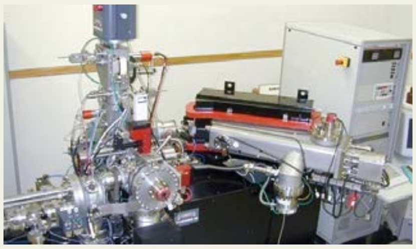
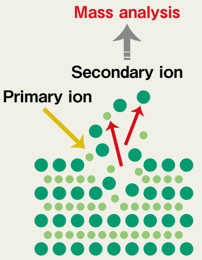


Figure 1. Sakaguchi uses an ultra-high spatial resolution secondary ion mass spectrometer, the NanoSIMS 50, capable of forming secondary ion images at high resolutions (50 nm or less) and high sensitivity.



General working principle of the SIMS

Isotopes are variants of particular chemical elements with different numbers of neutrons and thus different atomic masses. Oxygen has three known stable isotopes: ^{16}O, ^{17}O and ^{18}O, where the superscript numerals represent mass numbers.

To analyze oxygen defects in ceramics, a ceramic sample is first placed in a chamber filled with $^{18}O_2$ gas—an uncommon substance in nature—and then thermally treated. This leads to replacement of some of ^{16}O in the sample material with ^{18}O. SIMS analysis can then be used to determine the amount, pathway and speed of the incorporation of ^{18}O into the material. Based on this information, approximate quantities and locations of oxygen defects can be estimated.

“The information gathered using SIMS enabled me to improve the parameter settings, such as temperature and pressure, during ceramic synthesis,” said Sakaguchi. “As a result, we succeeded in creating ceramics highly sensitive to gases by adding optimum amounts of oxygen defects to them.”

Creating oxide thin films

In addition to enhancing the properties of gas sensitive ceramic materials, Sakaguchi is attempting to create ceramic thin films in an effort to reduce the size of gas sensors. The first step in creating thin films is to densely sinter raw materials. Argon gas is then allowed to collide with the sintered material, causing its components to be ejected and deposited on a substrate. Although some gas sensitive oxide raw materials are resistant to densification, it has been found that such materials can be densified by incorporating trace amounts of additives into them.

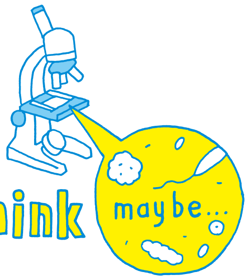
Sakaguchi prepared several sintered materials mixed with different amounts of additives. He then measured the concentration distributions of the additives and oxygen defects within each material sample using a SIMS. Finally, he transformed the materials into thin films and measured their gas sensing properties. As a result, Sakaguchi was able to determine the amounts of additives leading to the creation of dense sintered materials with desirable gas sensing properties.

The SIMS is a truly valuable tool for optimizing raw material choices and materials processing.

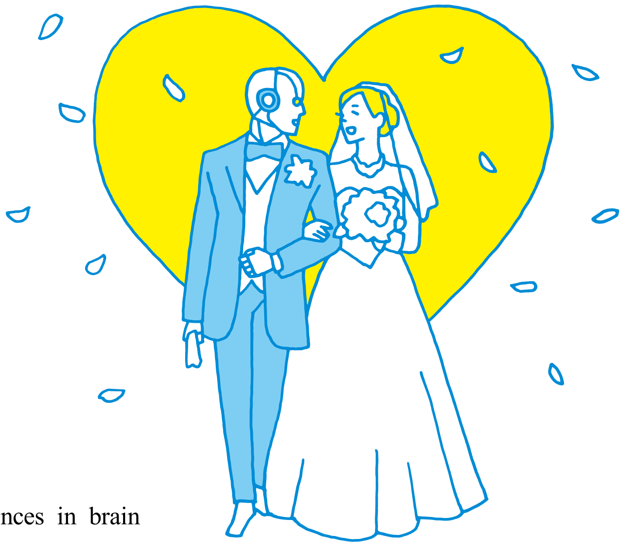
(by Shino Suzuki, PhotonCreate)

22

Science is even more amazing than you think



Harmonious coexistence of humans and artificial intelligence



Text by Akio Etori

Illustration by Joe Okada (vision track)

The development of artificial intelligence (AI) is progressing rapidly today. I have no doubt that AI will be integrated into our workplaces in the near future. Some may fear that their jobs will gradually be replaced by AI.

Dr. Yutaka Matsuo, Project Associate Professor at the University of Tokyo, recently made some interesting remarks about AI. He said that the integration of AI into society would give women an advantage over men. Work involving logic and calculation is often carried out by men, and this will eventually be taken over by AI due to its superiority in these areas. On the other hand, women are generally considered to be more empathic, a quality largely lacking in current AI technology. Therefore, women's roles will not be easily replaced by AI, according to Matsuo.

Empathy is important in a variety of social situations. It is certainly true that women occupy a majority of customer service and nursing positions, both of which require perception of others' needs.

Do clear differences really exist in the fundamental characteristics of the genders? If so, what causes them? I was fortunate to have the opportunity to raise these questions with Ms. Ihoko Kurokawa, an AI developer with expertise in brain science. According to her, the brain structures of the two genders are indeed different, which results in significant differences in brain function. She said that the differences are so large that it would be difficult to incorporate into the same AI systems.

What specific gender-related brain structure differences exist? Kurokawa said that the thickness of corpus callosum is a key difference.

The corpus callosum is a bundle of nerve fibers connecting the left and right cerebral hemispheres. Kurokawa explained that its thickness affects the extent of communication between the two hemispheres. Women have thicker corpus collosums than men, resulting in more developed communication.

The right cerebral hemisphere plays a vital role in perception, while the left brain controls the conscious mind's language functions. Kurokawa said that women with active interhemispheric communication are often proficient at perceiving the needs of others and flexibly responding to changes in situations.

On the other hand, men's brains, with less active interhemispheric communication, are capable of receiving information from sensory organs at sites scattered throughout the brain. This physiological characteristic generally gives men excellent spatial perception and goal-oriented thinking capabilities. According to Kurokawa, men with these attributes tend to take a logical approach to solving problems, while their empathic abilities are often inferior to those of women.

If all of this is true, Matsuo's prediction that AI will give women an advantage makes good sense.

Researchers around the world are currently engaged in fierce competition to develop robots capable of fluent communication. However, the development of such robots is expected to be a long-term endeavor due to the many challenges that must be overcome.

Several theories exist on the relationship between brain structure and function. Future advances in brain science may enable the development of AI capable of expressing empathy with humans. Such an achievement would bring major changes to our lives and values.

AI has the potential to become both a friend with whom you can share your worries and a rival in the workplace. If AIs with likable personalities can be developed, some may even accept them as life partners. Imagining the potential of AI makes me both anxious and excited.

Will AI with these assets actually be created? Will such AI really make our lives more affluent? Advancements in AI technology are generating many questions for us to think about.

Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

NIMS NEWS

1 NIMS researchers received HPCwire Readers' Choice Award

On November 13, 2017, NIMS has received an award with RIKEN AICS (Advanced Institute for Computational Science) from HPCwire at SC17 (International Conference for High Performance Computing Networking, Storage and Analysis) held at Denver, Colorado. This is the annual Readers' Choice Award conducted by HPCwire, to recognize the best and the brightest developments that happened in HPC (High Performance Computing) over the last 12 months. NIMS and RIKEN AICS received the “Best Use of HPC in Manufacturing” Readers' Choice Award for clarifying long-standing issues and advance development of next-generation batteries using K Computer.


From left: Keitaro Sodeyama (Senior Researcher, NIMS), Yoshitaka Tateyama (Group Leader, NIMS), and AICS Director Kimihiko Hirao (RIKEN)

2 NIMS Signed a Memorandum of Understanding with NIST

On February 1, 2018, Research and Services Division of Materials Data and Integrated System (MaDIS) of NIMS signed a memorandum of understanding with the Material Measurement Laboratory (MML) of the National Institute of Standards and Technology (NIST) ,US, to promote research exchange between the two organizations. Specifically, the two will collaborate on R&D related to advanced techniques for extracting data on materials using machine learning, develop data repository technologies to facilitate data collection, management and publication, and develop data platform technologies which will allow researchers to securely aggregate and store data. Through these broad collaborative efforts, the two organizations aim to establish de facto standards for data utilization policies and data management and promote open science by encouraging scientists in Japan and overseas to join the repository community.


NIST MML Director James Warren (left) and NIMS MaDIS Director Yuko Nagano (right)

Hello From NIMS


JSPS Dialogue talk
at Minami Iwata High School

Members of my group at NIMS


Autumn colours at Ryujin Suspension Bridge, Ibaraki

こんにちは(Konnichiwa)! My name is Geraldine, in 2015 I started a JSPS fellowship at NIMS. The climate and culture of Japan is vastly different from the UK, so settling into life here has been an enjoyable and enriching experience. With every season, there is a new thing to look forward to, I especially like the fireworks and festivals in summer. In my spare time, I go travelling to experience as much food and activities as possible. From Okinawa to Hokkaido I have found no two places to be the same, it is really interesting!

There are many researchers and institutes in Tsukuba, so it has the atmosphere of a ‘Science City’. During my fellowship, I delivered a lecture on nanomaterials at a high school. We did an activity where the students made slime (hydrogels), it was really enjoyable.

My research is focused on preparing new nanomaterials based on chiral perylenes. Whilst working at NIMS, I have been able to develop my skill as a scientist and enhance my knowledge of the world. I look forward to producing high-quality research outputs and continuing to make a contribution to science with my colleagues at NIMS.

Geraldine Echue (British)
Two Years in NIMS
Supermolecules Group, MANA

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http://www.nims.go.jp/eng/publicity/nimsnow/

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