MANA Research Digest 2017

World Premier International Research Center Initiative (WPI)
International Center for Materials Nanoarchitectonics (WPI-MANA)

National Institute for Materials Science (NIMS)

Preface

Takayoshi Sasaki
MANA Director
NIMS

The International Center for Materials Nanoarchitectonics (MANA) was established at NIMS in 2007 in the framework of the World Premier International Research Center Initiative (WPI program), which is sponsored by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT). Thanks to the great effort and support of many people over 10 years, we are proud that MANA has grown into a representative international research center in the fields of nanotechnology and material science, both in name and reality. MANA is pursuing innovation on the basis of our concept of "nanoarchitectonics", where new materials and functions are created by rationally integrating and organizing nanoscale parts. "Nanoarchitectonics" has now grown into a concept that is accepted around the world.

The 10 year WPI funding has ended in March 2017. Nevertheless, MANA will grow and develop further, and continue world leading research activities as an international hub institute for nanotechnology research. We are going to continue our efforts to deepen and pursue our "nanoarchitectonics". As one of seven research centers in NIMS and as a WPI center, MANA is engaged in a full range of research from basic to applied, in three research fields: Nano-Materials, Nano-Systems and Nano-Theory.

On behalf of all the researchers of MANA, I hope that the research activities described in this booklet will be a strong inspiration for your work in the future.

Nano Revolution
for the Future

MANA Research Digest 2017

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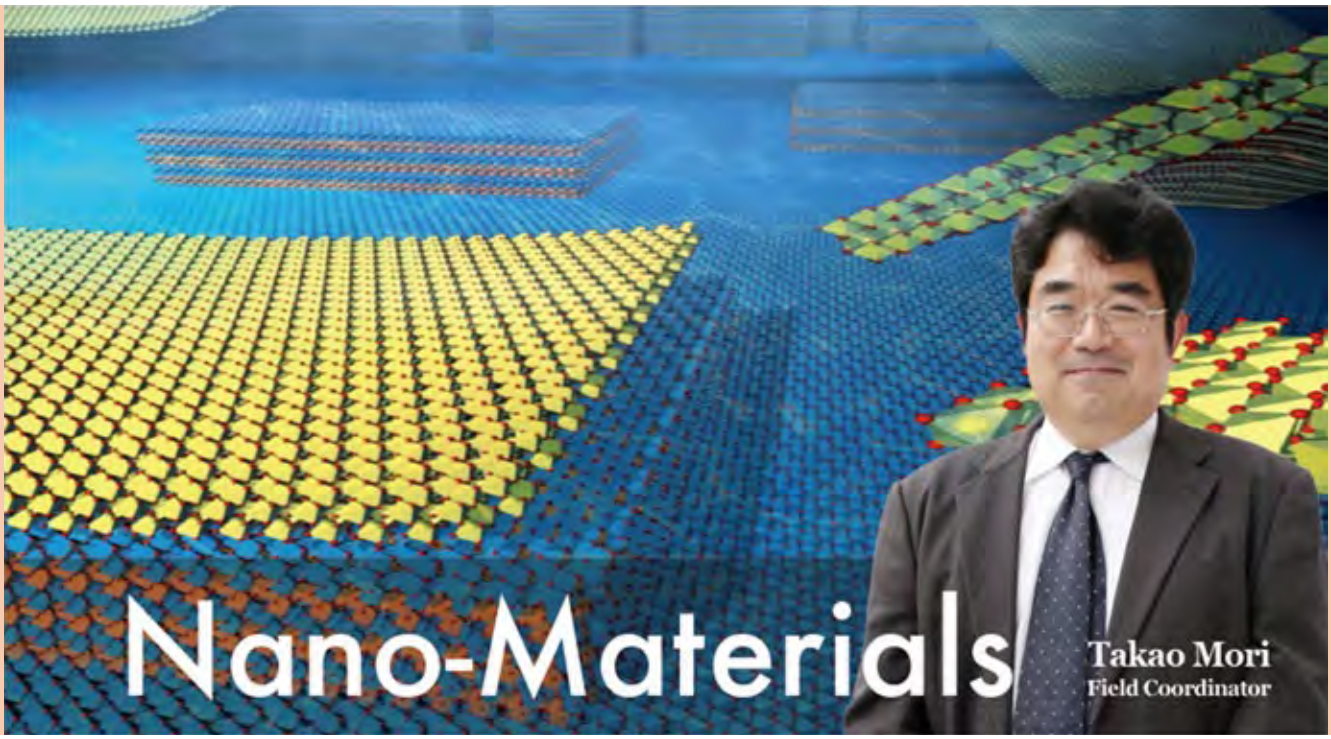

Creating new materials and eliciting novel functions by sophisticated control of compositions and structures at the nano level

Nano-Materials Field
(10 Research Groups)
- Thermal Energy Materials Group
- Soft Chemistry Group
- Supermolecules Group
- Semiconductor Device Materials Group
- Nanotubes Group
- Functional Nanosheets Group
- Mesoscale Materials Chemistry Group
- Photocatalytic Materials Group
- Nanostructured Semiconducting Materials Group
- Frontier Molecules Group

Making full use of MANA's advanced chemical synthesis technologies, beginning with soft chemistry, supermolecular chemistry and template synthesis, we are researching the creation of new nanomaterials such as nanotubes, nanowires, and nanosheets. Based on a wide range of material systems, spanning both organic and inorganic materials, we aim to discover novel physical properties and phenomena arising from size and shape in the nanometer range. MANA also develops and owns cutting-edge characterization facilities, including an integrated system of the transmission electron microscope with the scanning probe microscope, and is actively using these instruments for in-situ analysis of individual nanomaterials. In addition, we are promoting chemical nano- and mesoarchitectonics, in which these nanomaterials are precisely arranged, integrated and hybridized in the nano-to-meso range. By constructing artificial nanostructured materials in a designed manner, our aim is to create new materials that will exhibit advanced, innovative functions, and contribute to progress in a wide range of technological fields, including electronics, energy and the environment.

Thermal Energy Materials Group — Nano-Materials Field

Development of Thermal Energy Materials

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Rudder Wu (Senior Researcher), **Daiming Tang** (Researcher)

1. Outline of Research

Approximately two thirds of primary energy (fossil fuels, etc.) being consumed in the world, sadly turns out to be unutilized, with much of the waste being heat. It is imperative to develop better thermal management (insulators, thermal dissipation, etc.) materials. The direct conversion of waste heat to electricity is also a large incentive to find viable thermoelectric (TE) materials, and we are developing novel enhancement principles to functionalize abundant and safe element materials.[1-4)]

2. Research Activities

(1) Novel concepts for TE enhancement.

1A. Nano-micro pores for high ZT. Porous materials have typically yielded low thermoelectric performance with the detriment in electrical conductivity overcoming the decrease in thermal conductivity. As a new paradigm we have shown that a moderate amount of nano-micro pores can lead to excellent phonon selective scattering. Achieving a 100% enhancement of the figure of merit *ZT*, an unprecedented *ZT*~1.6 for rare earth-free skutterudites.[5)] In a completely different attempt, wet chemistry bottom-up synthesis of hollow-sphere nanoparticles led to an increase in ZT for oxides.[6)]

1B. Magnetic systems. We are also trying to enhance thermoelectrics with magnetism with the help of external funding. Recently clarified the importance of the interaction of the charge carrier and magnons.[7)] The enhancement through doping magnetic elements and magnetic interaction was also demonstrated.[8)] The metallic spinel sulfide system was universally considered to be low performance, but we have modified the magnetic $CuCr_2S_4$ system to have high ZT.[9)] Other magnetic thermoelectric systems were also investigated.[10)] Theoretical clarification of the phenomena also proceeded with predictions of enhancement of doped systems.[11)]

(2) Development of Thermal Measurements.

The capability to evaluate the thermal conductivity on a nanoscale is important for development of all thermal related materials, such as thermoelectric, thermal insulation, thermal dissipation (heat sink) materials. We have been utilizing picosecond thermoreflectance to measure nanofilms, and with a recently developed original focused system, site-selective measurements (Fig. 1) on microcrystals and inhomogenous or composite systems. For example, measurements on small crystals revealed that an inserted atomic layer (Fig. 2) functioned as an extreme phonon blocker, leading to unprecedently small thermal conductivity for a layered metallic boride (Fig. 3).[12)]

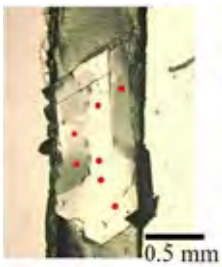

Fig. 1. Site-selective thermal conductivity measurements.

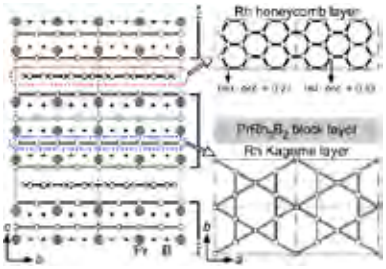

Fig. 2. Layered boride with Rh layer.

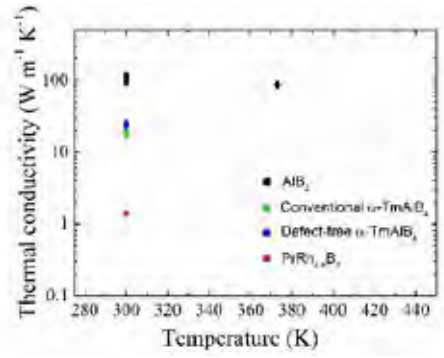

Fig. 3. Thermal conductivity of layered borides.

(3) Development of high temperature TE materials for topping cycles in thermal power plants.

Applications for high temperature TE materials including power plant topping was reviewed.[13)] Advancements have been made in the thermoelectric borides,[14,15)] oxides[16-18)] and nitrides.[19)]

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Soft Chemistry Group

Nano-Materials Field

Inorganic Nanosheets

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P. Xiong, X. Li, X. Lu (Research Associate)
Y. Song, L. Nurdiwijayanto, B. Xueyin, K. Inoue, H. Yano (Graduate Student)

1. Outline of Research

We aim at producing two-dimensional (2D) inorganic nanosheets as a unique class of nanoscale materials by delaminating various layered compounds through soft-chemical processes. Particular attention is paid to fine control of their composition and structure via doping and substitution of constituent elements, expecting new or enhanced properties. We develop a new nanofabrication process for precisely organizing colloidal nanosheets into multilayer or superlattice assemblies through solution-based processes (Fig. 1). Based on this novel approach with the nanosheets (soft-chemical nanoarchitectonics), we establish the tailoring ability and controllability over nanostructures with a precision down to 1 nm, which is comparable to that in lattice engineering utilizing modern vapor-phase deposition techniques. In the second stage, we take challenges to develop innovative nanostructured materials and nanodevices through nanoscale assembly of nanosheets and a range of foreign modules (organic compounds, metal complexes, clusters...). In particular, we attempt to realize new or sophisticated functions by cooperative interaction between nanosheets themselves or between nanosheets and other functional modules.

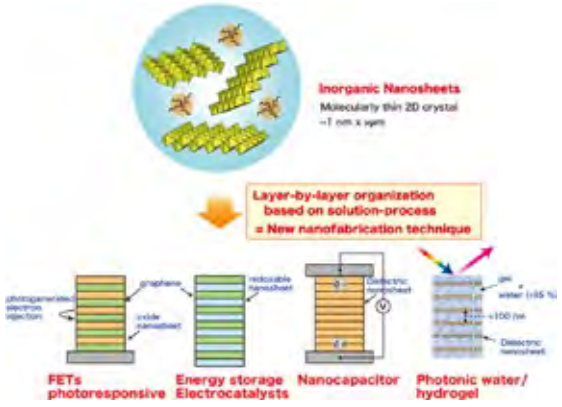

Fig. 1. Conceptual explanation of the research plan.

2. Research Activities

(1) New, facile and speedy technique for the film fabrication of neatly tiled oxide nanosheets .[1)]

We have demonstrated that neat monolayer tiling of various nanosheets ($Ti_{0.87}O_2$, $Ca_2Nb_3O_{10}$, GO, rGO) can be attained by spin coating their DMSO suspension under optimized conditions in terms of rotation speed and nanosheet concentration (Fig. 2a,b). Upon spin coating, nanosheets slide on the substrate surface under centrifugal force to the substrate end, where they are packed edge-by-edge all the way to the central region (Fig. 2c). The overlap is prevented due to the electrostatic repulsion between the nanosheets and the monolayer coverage reached >90%. The film quality is comparable to that of Langmuir-Blodgett deposition as the standard procedure for fabrication of high-quality nanosheet films, where the film thickness and architecture can be precisely controlled at nanoscale range. Repetition of the coating could lead to multilayer buildup. This process has advantages over the Langmuir-Blodgett method in terms of simple and facile operation and the short process time.

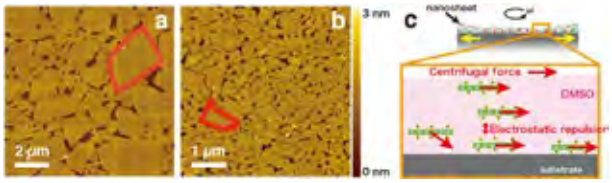

Fig. 2. AFM images of monolayer films of (a) GO and (b) $Ti_{0.87}O_2$ nanosheets. (c) schematic illustration of nanosheet tiling process.

(2) Exceptionally high hydroxyl ion conduction in layered double hydroxide (LDH) nanosheets.[2)]

We have successfully unveiled exceptionally high and anisotropic hydroxyl ion conducting behaviors in single-layer LDH nanosheets (Fig. 3a). Fig. 3b shows an AFM image of as-exfoliated nanosheets. After being deposited onto comb electrodes (Fig. 3c), in-plane hydroxyl ion conductivities were measured by ac impedance spectroscopy. As shown in Fig. 3d, the in-plane hydroxyl ion conductivity of LDH nanosheets reached 10^{-1} S/cm at 60 °C and 80% RH. The hydroxyl ion conductivity was the highest among anion conductors, even comparable to that of proton conducting membrane such as Nafion®.

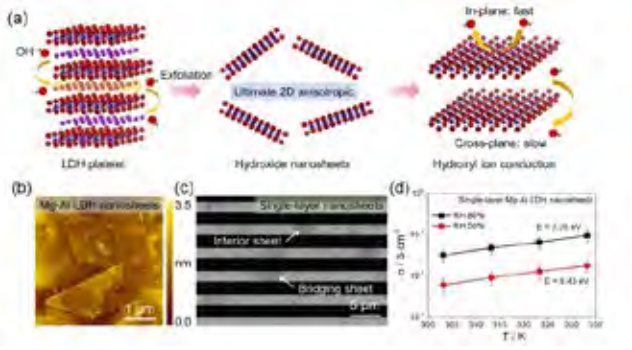

Fig. 3. (a) Schematic illustration of single-layer nanosheets and hydroxyl ion conduction. (b) AFM image of nanosheets. (c) SEM characterization of nanosheets deposited on comb electrodes. (d) Temperature-dependent in-plane hydroxyl ion conductivities of nanosheets at different RH.

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Supermolecules Group

Nano-Materials Field

Supramolecular Materials

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1. Outline of Research

Functional materials have been wisely constructed via bottom-up approaches as seen in preparation of molecular and nano patterns, complexes, and nanomaterials organized nano- and microstructures, and function materials. We are working in exploratory research for innovative materials and sensing systems based on supramolecular concepts.[1-7]

2. Research Activities

(1) Nano: Driving soft molecular vehicles.

We synthesized and characterized a conformationally flexible molecule consisting of two binaphtyl paddles mounted on a simple phenyl chassis.[5] The vibration modes of the lateral paddles can be exploited to induce the motion of the molecule on an Au(111) surface using STM inelastic tunneling effects (Fig. 1). On the metallic surface it is possible to switch molecules, one at a time, to a flat configuration using a specific STM mechanical manipulation protocol. In April 2017, a nanocar race took place, in which several molecular machines synthesized by groups from around the world competed with the goal of covering a set distance on a gold surface in the minimum possible amount of time, driven by STM tips.

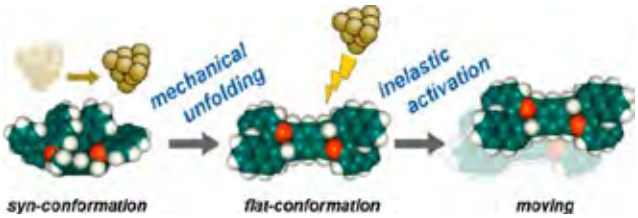

Fig. 1. Control of a molecular car by a STM tip.

(2) Materials: Pockets in fullerene cube.

We recently succeeded in fabricating micro-sized cubes using a carbon material, C_{70} fullerenes, with a pore. with approximately 1 μm deep in every face of the cubes using a dynamic LLIP method, a modified LLIP (liquid-liquid interfacial precipitation) method (Fig. 2).[3] The opening and closing of the pores can be controlled easily. Among two types of similarly-sized particles (resin- and carbon-based particles), the cubes were capable of responding to the chemical properties of the two particles and allowed many carbon-based particles to enter their pores while preventing all but one resin-based particle from entering.

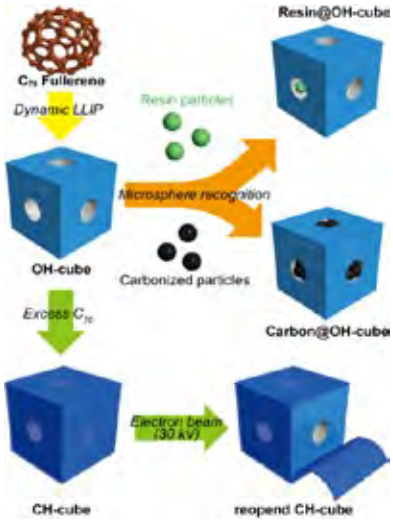

Fig. 2. Manipulation pf fullerene cube.

(3) Bio: Cell differentiation control on a liquid surface.

We demonstrate the regulation of myogenic differentiation on fluid substrates by using a liquid-liquid interface as a scaffold (Fig. 3).[4] Furthermore, we successfully transferred the cells cultured at such interfaces using Langmuir-Blodgett (LB) techniques. The combination of the interfacial culture system with the LB approach enables investigation of the effects of mechanical compression on cell functions. Our results offer the potential utility of the interfacial culture system for investigation of the effects of mechanical forces on cells to the fields of tissue engineering and stem cell research as well as to the field of mechanobiology.

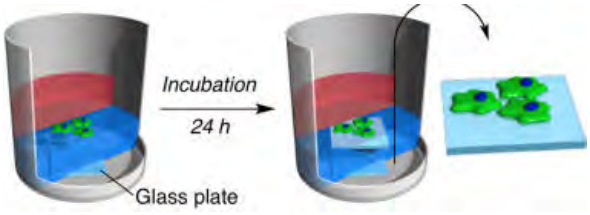

Fig. 3. Cell culture at liquid-liquid interface.

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Semiconductor Device Materials Group

Nano-Materials Field

Nano Electrics and Related Materials

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1. Outline of Research

In order to achieve further progress in MOS devices, high-mobility semiconductors and a high dielectric constant (high-k) materials are essential. Ge is a candidate next-generation channel material to improve MOS gate structures in terms of high electron and hole mobilities.[1,2] The effects of Y and Mn doping into the rutile TiO_2 films on a (100) Ge substrate stack structure were investigated by combinatorial synthesis. Composition spread films were fabricated by combinatorial pulsed laser deposition. Regardless of the dopant concentration, the Mn-doped TiO_2 film indicated an amorphous structure. In contrast, the Y-doped TiO_2 film had a rutile-type crystal structure below an Y concentration of 11.0 at%. The high Y concentration enhanced the amorphous structure and Ge diffusion into the TiO_2 layer. Although both dopants reduced leakage currents, the effect of Y was greater than that of Mn. The post-deposition annealed Y-doped TiO_2 indicated an improvement in the leakage current by three orders of magnitude and electron accumulation at a capacitor structure. The Y doping into TiO_2 may provide beneficial effects of good interface control and effective dielectric material for Ge-based capacitors.[3]

2. Research Activities

The acceptor-doped TiO_2 film was prepared by PLD and the combinatorial method using sintered ceramic TiO_2, Y_2O_3, and MnO_2 targets. Samples with a film thickness of 30 nm were fabricated under the following conditions: an O_2 partial pressure of 1.3×10^{-3} Pa, a substrate temperature of 450 °C, and a laser density of 0.7 J·cm^{-2}. A 100-nm-thick Pt top electrode with a diameter of 150 μm was deposited on the samples by DC sputtering using a shadow mask. Oxygen ambient post-deposition annealing was performed at 400 °C for 30 min. Crystal structures were analyzed by two-dimensional X-ray diffraction (2D-XRD) measurement with a 5kW rotating anode, a Cu target, and a high-resolution 2D detector(Bruker AXS D8 Discover Super Speed with GADDS). The chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS) using a monochromated Al Kα X-ray source with a spot size of 400 μm.

Fig. 1(a) shows the 2D-XRD pattern of 2.2 at% Y-TiO_2. This image exhibited spots corresponding to the (110) reflection from the rutile structure at $2\theta = 27.3°$. X-ray pole figure measurements revealed that the (110) TiO_2// (001) Ge and [100] TiO_2 // [100] Ge with a 90°-rotated domain (not shown) Fig. 1(a) shows 2θ–ω scan XRD patterns for Y-TiO_2. With increasing dopant concentration, the intensity of the (110) reflection corresponding to the rutile phase decreased, and amorphous phases were observed above a Y concentration of 11.0 at%. Note that, regardless of the Y concentration, no refraction corresponding to oxide components of the dopant, such as Y_2O_3, was confirmed, indicating that there is no clear phase separation in any sample. In contrast, Mn-TiO_2 showed an amorphous structure at all concentrations, as shown in Fig. 1(b) shows the J–V characteristics of 11 at.% Y-TiO_2 after post-deposition annealing. Combined with the results by XPS measurement, the improvement in the leakage current was found that it should correspond to not the crystallization but the oxygen vacancy density.

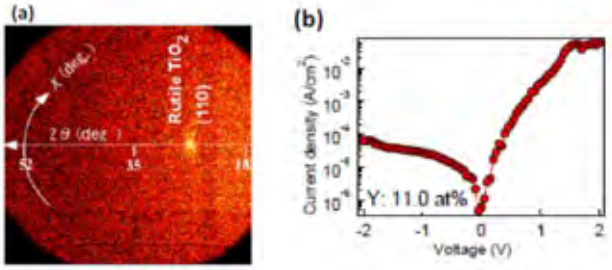

Fig. 1. (a) 2D-XRD pattern Y-doped TiO_2 on Ge substrate. An epitaxial growth of rutile TiO_2 was observed. (b) J-V characteristic of the Y-doped TiO_2. Leakage current was successfully suppressed.

As the summary, to improve the electrical properties of the rutile-type TiO_2/Ge stack structure, Y and Mn doping was investigated by combinatorial synthesis. Y doping was more effective in improving the leakage properties than Mn doping. For the crystallization of TiO_2, Y inhibited the rutile phase formation and crystallization.

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Semiconductor Device Materials Group — Nano-Materials Field

Characterization and Control of Defects

Managing Researcher **Takashi SEKIGUCHI**

Toyohiro Chikyow (Group Leader), **Jin Kawakita** (Chief Researcher), **Michiko Yoshitake** (Chief Researcher), **Shinjiro Yagyu** (Principal Researcher), **Yoshiyuki Yamashita** (Principal Researcher), **Jun Chen** (Senior Researcher), **Takahiro Nagata** (Senior Researcher)

1. Outline of Research

We have been pursuing 4 projects for semiconductors named "Square Si," "Multi-dimensional EBIC," "Anything CL," and "100V EM". "Defect Control" is the key issue for these projects. We are characterizing various properties of defects in nanoscale. For this purpose, we have developed special electron beam characterization techniques, such as electron-beam-induced current (EBIC) and cathodoluminescence (CL) as well as the secondary electron (SE) imaging. First, we have improved the spatial resolution of EBIC/CL by introducing a better electro-optics and optimizing the light collection system. Second, the new specimen preparation techniques, such as cross sectional polisher (CP) and focus ion beam (FIB) have been introduced.

2. Research Activities

(1) Characterization of pn junction in GaN (Anything CL).

Precise doping control is of critical importance in GaN power device fabrication. In this study we characterize pn-junctions of GaN by using cross sectional CL method.[1] To improve spatial resolution, the specimens were obliquely polished using cross sectional polisher. The vertical structure of GaN pn junction is shown in Fig. 1(a) as well as SE image of its oblique cross section (b). The CL spectral variation along the yellow line is shown in (c). The donor-accepter pair emission (2.8-3.2 eV) is observed in p-type region, while band edge emission (3.44 eV) is dominant in n-type region. The detailed analysis of CL spectra gives the information of both activated and inactivated Mg impurities.

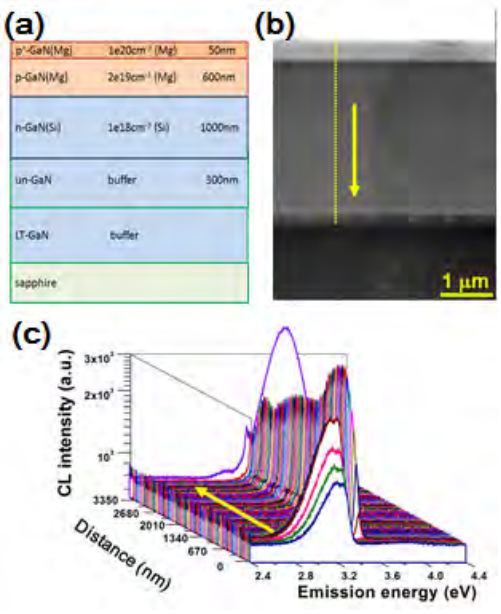

Fig. 1. (a) GaN pn junction structure, (b) SE image of oblique cross section, (c) CL spectra along yellow line. 3 kV, 80 K.

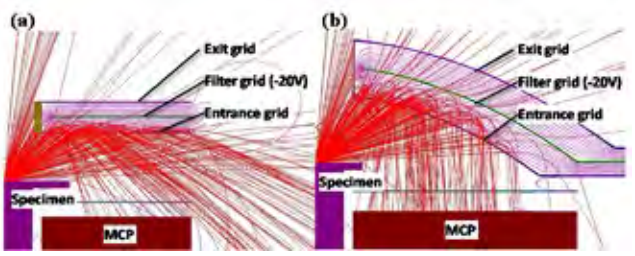

Fig. 2. SE trajectory simulation for FDs: (a) planner type; (b) spherical type; the filter grid was set at -20V. red and pink lines represent SE trajectories and equi-potential lines, respectively.

(2) Fountain Secondary Electron Detector (100V EM).

Scanning electron microscopy (SEM) is now indispensable for nanotechnology and nanoscience. To image the variation of surface potential in semiconductors, energy selective secondary electron detector, named fountain detector (FD), was developed.[2] Two types of grids, planar and spherical, were designed and the superiority of latter was demonstrated (Fig. 2). The p-n junction of 4H-SiC was observed using spherical FD and the image was much clear than that using conventional detector (Fig. 3).

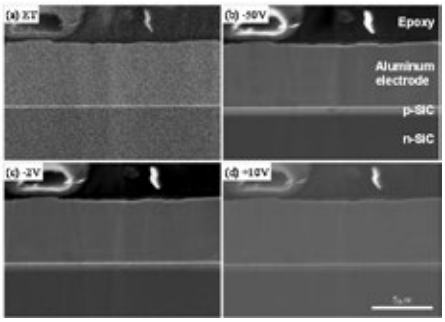

Fig. 3. SEM images of a 4H-SiC p-n junction: (a) an SEM image taken by a ET detector; (b-d) SEM images taken by the spherical FD with the filter bias of -50V, -2V and +10V, respectively.

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Nanotubes Group

Nano-Materials Field

Nanowire, Nanotube and Nanoparticle Properties: *In situ* TEM Thermal Measurements

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Naoyuki Kawamoto (Senior Researcher)

1. Outline of Research

Increasing levels of miniaturization in today's nanoscale devices bring about new problems which have to be overcome.[1,2] Heat is the limiting factor which governs the performance of current electronic circuits. Understanding local temperature distributions and heat transport is of paramount importance, but measuring these quantities at the nanoscale is non-trivial. Our research aims to probe these quantities by integrating various measurement techniques inside a TEM, towards the ultimate spatial resolution.

2. Research Activities

(1) Nanoscale thermal transport analysis by STAM.

We developed and demonstrated scanning transmission electron microscopy (STEM)-based thermal analytical microscopy (STAM) by combining nanoscale temperature measurements using the world-smallest thermocouple[3] with the ultimately high temperature resolution (more than three orders of magnitude better than during any previous conventional nanoscale temperature measurements in a transmission electron microscope) with a scanning heat input through focused electron beam irradiation using STEM mode (Fig. 1). By using this method, we succeeded in visualizing heat distribution maps (as STAM images) for a practical heatsink composite and advanced thermoelectric materials where complicated heat flow took place at the nanoscale.

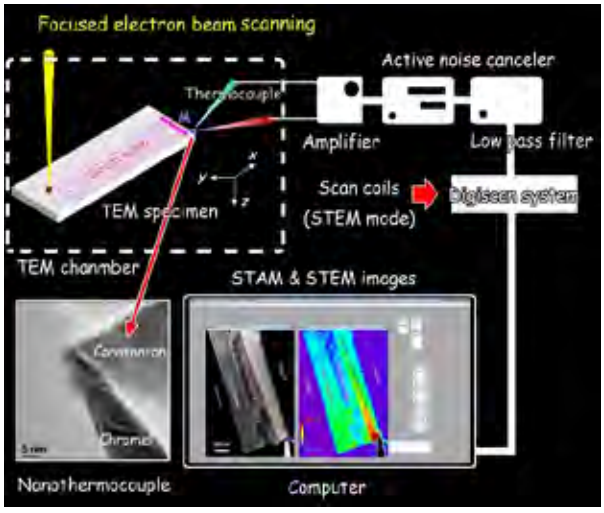

Fig. 1. Scheme of experimental configuration for STAM measurements under two-dimensional thermal analysis.

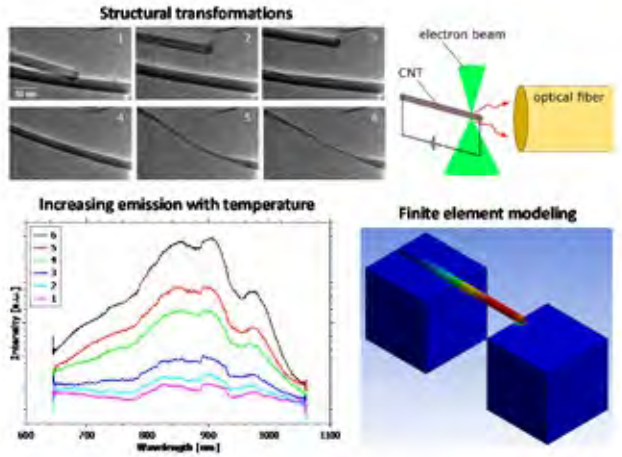

Fig. 2. Schematic and experimental results in regard of nanotube temperature measurements using an optical fiber placed in TEM.

(2) Nanotube temperature measurements inside TEM.

Carbon nanotubes show promise as the ultimate interconnects, due to their ability to withstand significant mechanical, electrical and thermal constraints. The degradation of individual nanotubes during electrical transport has been observed numerous times, but the underlying mechanism is not properly understood. Given the high injection levels, Joule heating is expected to be the primary mechanism. There is a need to better understand the behavior of individual nanotubes undergoing this process. While electrical properties can be easily obtained, the same thing cannot be said for the temperature of these objects.

Our approach is based on the results in which we have shown that optical signals can be obtained from individual nanoscale objects inside the TEM, by positioning an optical fiber in very close proximity[4] (Fig. 2). We extend this method by combining it with electrical transport measurements, performed simultaneously on the same object. The results show that we are able to successfully sense temperature variations in individual nanotubes, while correlating them with structural and electrical properties.

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Functional Nanosheets Group

Nano-Materials Field

Nanosheet Electronics

Principal Investigator* **Minoru OSADA**
(Group Leader*)
Takashi Aizawa (Chief Researcher), **Takaaki Taniguchi** (Senior Researcher)
*Until December 2017

1. Outline of Research

Two-dimensional (2D) nanosheets, which possess atomic or molecular thickness, have been emerging as important new materials due to their unique properties. The ultrathin thickness and high flexibility of 2D nanosheets render them appealing building blocks for constructing new electronics. Graphene is one of the most promising materials being researched today; it has many amazing functionalities such as high electron mobility, prompting researchers to suggest that graphene will one day replace silicon in electronic devices. However, graphene is a conductor, and electronic technology also requires insulators and semiconductors. Along with graphene, 2D inorganic nanosheets have increasingly attracted fundamental research interest because of their diversity in physical properties. Among the type of 2D inorganic nanosheets, oxide nanosheets are important, fascinating research targets to be pursued because of the virtually infinite varieties of layered oxide materials with interesting functional properties. We are working on the creation of 2D oxide nanosheets and the exploration of their novel functionalities in electronic applications.

2. Research Activities

(1) Atomic Layer Engineering of 2D Perovskites.

Complex perovskite oxides offer tremendous potential for controlling their rich variety of electronic properties including high-T_C superconductivity, high-k dielectric/ferroelectric, and quantum magnetism. We demonstrated atomic-scale engineering of dielectric responses using 2D perovskite nanosheets ($Ca_2Na_{m-3}Nb_mO_{3m+1}$; m = 3–6) (Fig. 1).[1] In this unique system, perovskite nanosheets allow us to achieve precise control over the thickness of the perovskite layers in increment of ~0.4 nm (one perovskite unit) by changing m, and such atomic layer engineering enhances the high-k dielectric response. The end member ($Ca_2Na_3Nb_6O_{19}$; m = 6) attained the highest dielectric constant (ε_r = ~470) ever realized in all known dielectrics in the ultrathin region (< 10 nm). These results provide new strategy for achieving high-k dielectrics for use in ultra-scaled high-density capacitors and post-graphene technology.

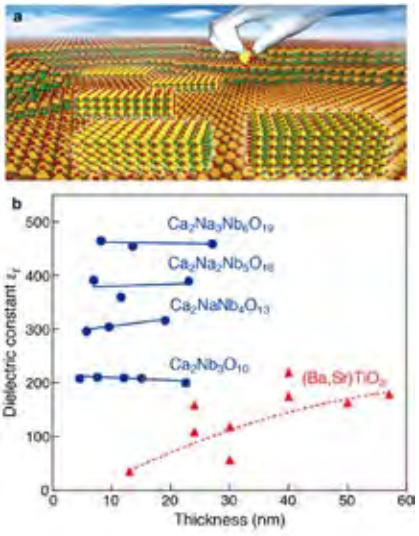

Fig. 1. (a) Atomic layer engineering and (b) dielectric properites of perovskite nanosheets ($Ca_2Na_{m-3}Nb_mO_{3m+1}$; m = 3–6).

We extended our research to various electronic/energy devices.[2,3] Perovskite nanosheets exhibited outstanding energy storage capabilities, even comparable to that of Li-ion battery. Another enticing possibility is the heteroassembly of conducting/high-k nanosheets. Such a superlattice will allow the rational design of high-performance FET devices, which may realize mobility enhancement by dielectric screening.

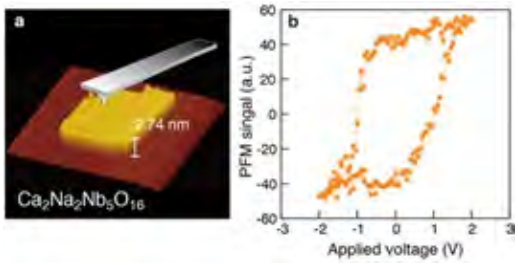

Fig. 2. (a) AFM image and (b) piezoresponse of $Ca_2Na_2Nb_5O_{16}$ nanosheet.

(2) Room-Temperature Ferroelectricity in 2D Perovskites.

2D materials have emerged as promising candidates for various electronic applications based on their diverse electronic properties. However, cooperative phenomena such as ferroelectricity in the 2D limit have not been well explored. We discovered room-temperature ferroelectricity in perovskite nanosheet ($Ca_2Na_2Nb_5O_{16}$) (Fig. 2).[1] Switchable polarization (P_s = ~20 μC/cm^2) was observed in the thickness down to 3 nm. The addition of ferroelectricity to the 2D family opens possibilities for numerous novel applications, including sensors, actuators, non-volatile memory devices, etc.

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Mesoscale Materials Chemistry Group

Nano-Materials Field

Hierarchical Porous Carbons

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Cross Appointment with University of Wollongong, Australia
Joel Henzie (Senior Researcher), **Yusuke Ide** (Senior Researcher),
Satoshi Tominaka (Senior Researcher)

1. Outline of Research

One possible method to prevent the restacking of nanosheets is to prepare crumpled or curved nanosheets, which creates spacings when packed together; however, the accessibility of the parallel channels is impaired. Another strategy is to grow 2D nanosheets vertically aligned to the substrate by chemical vapor deposition (CVD) method; although the parallel planar channels are well-maintained, the deposited amount of 2D nanosheets per unit area is restricted, thus limiting the performance. The third approach consist in incorporating small dimensional nanoparticles or molecules (*e.g.* 0D carbon onions or quantum dots, 1D carbon nanotubes, 2D carbon nanosheets, and polymers) within the interlayers, acting as spacers between the 2D nanosheets. Most of the heterostructures are built on van der Waals forces which allow the free integration of 2D nanosheets with disparate nanomaterials. However, this strategy results in the nondirective and non-uniformly distributed interlayer spacers in host materials, which leads to a complex interlayer pathway for ion diffusion and/or electron transfer. Thus, it is still a great challenge to build regular, rigid, porous, and electron conductive bridges between the nanosheets, while preventing their restacking and promoting mass transportation.

In our group, as a proof of concept, we fabricated 2D-2D heterostructures by designing the intercalation of 2D ordered mesoporous carbon (OMC) thin layers within the MXenes interlayer spaces (Fig. 1). The 2D OMC intercalated between the MXenes layers not only prevents the restacking of the nanosheets but the highly interconnected nanoporous network also provides accessible pathways for ion diffusion while maintaining fast electron transfer. The concept proposed here will open a new paradigm for the synthesis of 2D hybrid nanomaterials and broaden the range of applications of 2D nanomaterials.[1,2)]

2. Research Activities

This work proposed to prepare 2D-2D heterostructured composites which are assembled by 2D $Ti_3C_2T_x$ (or $Ti_3C_2T_x$-derived MDC) nanosheets and 2D ordered mesoporous carbon layers. The key points of this strategy are to prepare 2D nanosheets host with abundant hydrophilic surface termination, and control the molecular weight of guest organic molecules and block copolymers to allow their easy intercalation within the narrow interlayer space, then confine the close-packing assembly of block copolymer micelles. The thickness of the intercalated OMC layer is dependent on the interlayer distance of the 2D host due to the confinement

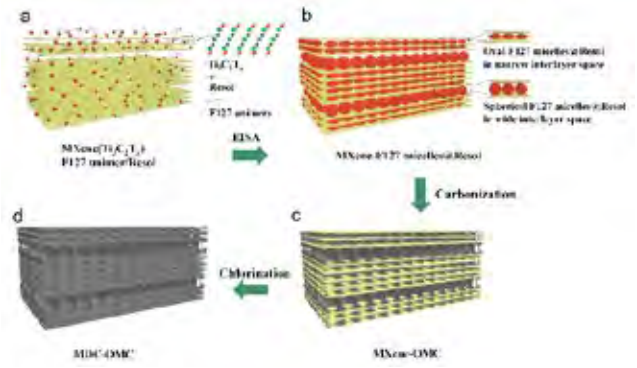

Fig. 1. The preparation of the MXene-OMC and MDC-OMC composites.

effect. When used as electrode for supercapacitor, the $Ti_3C_2T_x$-OMC and MDC-OMC samples exhibit superior performance than the pristine 2D materials. The improved capacitive performance should be attributed to the synergetic effects of the 2D-2D heterostructure. The interconnected structures consisting of 2D nanosheets and mesopores allow easier ion transport to reach the electroactive sites in the bulk materials and enhance the utilizations of electrodes, giving rise to an increased capacitance. The aligned mesopores can also serve as an electrolyte reservoir, which significantly shorten the diffusion paths and improve the transport efficiency. In addition, the mesoporous carbon intercalated in the layers provides a continuous electron pathway between two adjacent MDC sheets (*c*-direction), ensuring good electrical conductivity.

This work paves a pathway for solving the stacking and connection problem in 2D nanosheets by constructing regular, vertical, and accessible porous pillars within the 2D interlayers. This versatile approach can be expected to be further adapted for the direct patterning of mesoporous carbon on the surface of 2D materials. From the view of practical application, the concept proposed here, nanofabrication of vertical accessible pillars inside 2D layers, will open a new paradigm for the synthesis of 2D hybrid nanomaterials to target a broad variety of applications. In further research, this strategy can be extended to prepare other 2D-2D hybrid materials.

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Photocatalytic Materials Group

Nano-Materials Field

Hybrid Artificial Photosynthetic System

Principal Investigator **Jinhua YE**
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Mitsutake Oshikiri (Principal Researcher), **Tetsuya Kako** (Senior Researcher)

1. Outline of Research

We are conducting research and development of novel photocatalytic materials for a more efficient utilization of solar energy, as well as application of these materials for degradation of hazardous organics, solar hydrogen production and CO_2 conversion to useful hydrocarbon fuels. Our research approaches mainly include composition- and morphology-controlled fabrication of nanometals, organic/inorganic semiconductor materials and integration of those materials for advanced utilization of sunlight and efficient conversion to chemical energy. Also, through conducting fusion researches between theoretical calculations and in-situ measurements, we are elucidating reaction mechanisms in order to provide crucial design guidelines for new material development, and lead to the discovery of new principles and functions. For more details, we are conducting (Fig. 1):
1) Design and fabrication of new semiconductors which can utilize solar energy sufficiently by energy band structure engineering, with the help of theoretical calculation basing on the first principle theory.
2) Nanoarchitectonics of the photosynthetic system by not only fabrication of nano particles using various soft chemical method, but also assembling of nano-metal/nano-oxide hybridized system to achieve efficient transportation and separation of electron-hole charge carriers.
3) Mechanism study by experimental and theoretical approaches, to establish guidelines for development of higher efficient system.

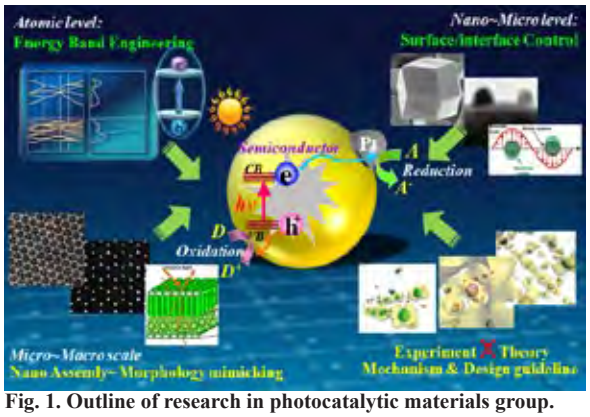

Fig. 1. Outline of research in photocatalytic materials group.

2. Research Activities

(1) Solar-driven nitrogen fixation in pure water for hydrogen energy storage. [1)]

Inspired by oxygen vacancies (OVs) could enhance the adsorption and activation of N_2. Recently we have designed a self-assembled 5-nm-diameter Bi_5O_7Br nanotubes with confined nanotube structure, suitable absorption edge, and a plethora of exposed surface sites furnished with sufficient visible light-induced OVs (Fig. 2). It results in the NH_3 generation rate as high as 1.38 mmol h^{-1} g^{-1} and an apparent quantum efficiency over 2.3 %. We also revealed that, under visible light irradiation, partial O atoms will escape in the form of O_2 from the surface of ultrafine Bi_5O_7Br nanotubes so that create sufficient surface OVs as reaction centers, which are responsible for the excellent photocatalytic N_2 fixation activities. It provides new insights into the creation of OVs on semiconductors towards efficient, stable and sustainable visible light N_2 fixation for energy storage.

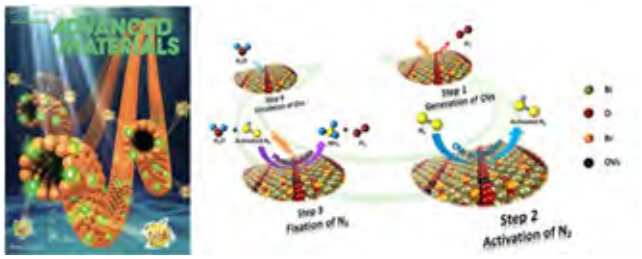

Fig. 2. Left: Image of the Light-switchable OVs on Bi_5O_7Br nanotubes for N_2 fixation. Right: The reversible creation of light- induced OVs. [1)]

(2) Dual purpose strategy for solar-driven activation of molecular oxygen. [2)]

We have combined the action of carbon doping and ultrathin structure on Bi_2MoO_6, thus exhibiting a promoted redox ability without losing any absorption of solar light, an internal electric field and shorten distance in the direction of charge transfer (Fig. 3). The long-term NO removal activities over the ultrathin C-doped Bi_2MoO_6 nanosheets was 4.3 times higher than that over the bulk counterparts as a result of the increasing reactive oxygen species ($\bullet O_2^-$, $\bullet OH$, $^1O_2$). It realized the band structure engineering and charge transportation regulation for activation of molecular oxygen.

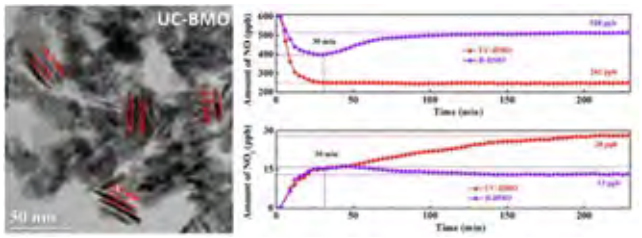

Fig. 3. Left: HRTEM images of the ultrathin C-doped Bi_2MoO_6 photocatalyst. Right: Long-term NO removal activities for ultrathin C-doped Bi_2MoO_6 and bulk counterparts. [2)]

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Nanostructured Semiconducting Materials Group — Nano-Materials Field

Next-Generation Semiconductor Nanodevices

Group Leader **Naoki FUKATA**

Wipakorn Jevasuwan (Researcher), **Ryo Matsumura** (Researcher)

1. Outline of Research

Very recently, non-radiative energy transfer (NRET) has been proposed for hybrid nanostructures that combine absorbing components (e.g., quantum dots, nanocrystals).[1,2] We predict this will open new possibilities in light harvesting. Use of 0-dimentional colloidal semiconductor nanocrystals in these hybrids provides the advantage of absorbing a wider range of the light spectrum than Si layers are able to; and exploiting the NRET process can overcome the limitations of low charge transfer efficiency in charge transfer-based devices. Long-range dipole-dipole interaction in NRET hybrids can exceed both short range charge transfer and radiative energy transfer.[1,2] The experimental evidence has been observed in hybrid semiconductor heterostructures under optical excitation between a single semiconductor nanostructure and an adjacent layer of organic molecules or colloidal CdS, CdSe and PbS quantum dots.[1-3] As concerns toxicity, Si nanocrystal quantum dots (nc-Si QDs) offer a promising alternative to the heavy metal-containing compound semiconductor quantum dots currently used in studying NRET hybrids. Si nanocrystals (diameter < 5 nm), due to the confinement effect and depending on their encapsulating ligands, are able to emit in visible frequencies after absorbing the light spectrum.

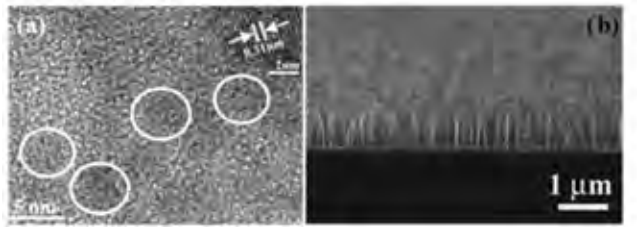

Fig. 1. (a) High-resolutional TEM images of nc-Si QDs. (b) SEM image of SiNW array formed on n-Si substrate.

2. Research Activities

(1) Formation of Si nanocrystal quantum dots (nc-Si QDs) and Si nanowires (SiNWs).

nc-Si QDs were synthesized from hydrogen silsesquioxane (HSQ). The surface was terminated by 1-octadecene. SiNW arrays were formed on n-type Si substrates by metal-catalyzed electroless etching (MCEE) using a solution of 0.02 M $AgNO_3$ in HF (4.6 M). The TEM image of nc-Si QDs and the SEM image of SiNWs are shown in Fig. 1.

(2) Demonstration of non-radiative energy transfer (NRET).[4]

nc-Si QDs deposited by spin coating on the top of poly p-Si layer transfer energy to the Si layers beneath both radiatively and non-radiatively. Charge transfer is facilitated by the electronic wave functions overlap with exponential dependence on the distance in angstrom-size scale. Therefore the probability of charge transfer from the nc-Si QDs to the Si layer beneath can be ignored, since the nc-Si QDs are well covered by insulating ligands ~2 nm in length and separated by a 1 - 2 nm-thick SiO_2 layer from the beneath Si layer. Time dependent photoluminescence (PL) decays of the colloidal nc-Si QDs on the p-Si layer with the hybrid radial p-n junction were measured and compared with that of nc-Si QDs on a glass substrate to characterize the efficiencies of radiative and non-radiative energy transfers in the hybrid structure. Comparison of the two PL decay curves clearly revealed the presence of an extra energy transfer channel in the hybrid structure, as shown in Fig. 2. The single and bi exponential fits of the PL decays yield respective PL lifetime of nc-Si QDs on glass as τ_{glass}=29.24 μs and on p-Si layer τ_{hybrid} = 6.27 μs (for the fast component of the decay) and 27.58 μs (for the slow component of the decay). The close similarity in slow components of the PL decays suggests that inter dot transfer mechanisms remain the same in the hybrid structure. The PL decay of nc-Si QDs on the glass substrate is dominated by the radiative and intrinsic non-radiative recombination channels (if any). However, in the hybrid structure, non-radiative energy transfer along with radiative energy transfer to the p-Si layer contributes to the nc-Si QDs PL decay rate as an extra energy transfer channel. We could estimate the radiative and non-radiative recombination lifetime to be 20.9 μs and 12.9 μs, respectively. The non-radiative energy transfer rate is therefore ~ 1.6 times faster than radiative energy transfer rate to the underlying Si layer. Our data demonstrated the possibility of non-radiative energy transfer from nc-Si QDs.

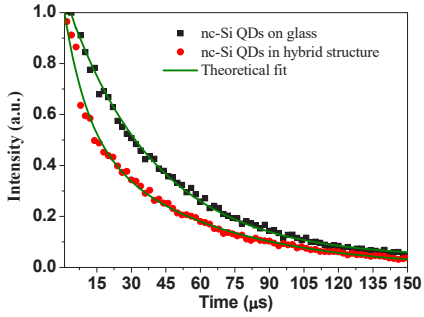

Fig. 2. Time-resolved PL of nc-Si QDs on glass and in the hybrid structure at a detection wavelength of 625 nm.

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Frontier Molecules Group

Nano-Materials Field

Exotic and Functional Molecular Materials

Group Leader **Takashi NAKANISHI**

Kentaro Tashiro (Principal Researcher), **Shinsuke Ishihara** (Senior Researcher)

1. Outline of Research

As the second year of Frontier Molecules Group established, we are working on synthesis of unique and frontier molecules possessing advanced functions and uncommon phenomena towards applications in sensor, actuator as well as bio-medical usage. Our research contains original molecular design strategy, synthesis, self-assembly, molecular recognition and hybridization with inorganic or bio-nanomaterials. We are aiming at development of world-top-level functional molecular systems/materials with our original molecules.[1-7)]

2. Research Activities

(1) Unexplored liquid matter.

The very recent development of solvent-free, nonvolatile, room temperature functional molecule liquids (FMLs)[1)] has created an increasing debate on a clear boundary between liquid crystalline fluids and isotropic liquids. Alternation of number and substitution pattern of bulky and flexible branched alkyl chains on a blue-color luminescent pyrene[2)] or naphthalene[3)] unit allows us to study deeper insight of π-π interactions in their neat liquid state. Through investigation on photophysical properties of the alkylated-π liquids illustrated homogeneity (monomer emission) or inhomogeneity (excimer emissions) in those liquids depending on the extent of π-unit isolation with attached alkyl chains[2)] and/or inherent electronic structure of compounds (Fig. 1).[3)] Our new findings have revealed an unexplored liquid matter that lies exactly between relatively disordered liquid crystalline fluids and totally-disordered isotropic liquids.

(2) Aerogel photocatalyst.[4,5)]

Physical adsorption of various metal complexes including multinuclear heterometallic species onto polymethylsilsesquioxane (PMSQ) aerogel successfully afforded their highly transparent mesoporous hybrids. One of the fabricated materials containing a Ru(II) tris-phenanthroline complex exhibited a photo-catalytic activity for the dehydrogenation of Hantzsch 1,4-dihydropyridine even close to that observed for the corresponding homogeneous system. The photo-catalytic activity of the aerogel catalyst was superior than that of the same metal complex on other silica gels having larger or smaller pores, suggesting that the pore size of the PMSQ aerogel plays the important role for the high photo-catalytic activity by allowing both of the light and substrates to easily access the catalysts located at the inner space of the material.

(3) Toxic gas sensor made from polymer-wrapped nanotube.

As-synthesized single-walled carbon nanotubes (SWCNTs) are a mixture of metallic and semiconducting tubes, and separation is essential to improve the performances of SWCNTs-based electric devices. We reported that a finely-isolated semiconducting SWCNTs network, wherein each tube is wrapped by insulating metallo-supramolecular polymer (MSP), demonstrates significant increase in conductivity (up to 100 times) when vapors of strong electrophiles such as diethyl chlorophosphate (DECP), a nerve agent simulant, trigger disassembly of MSP.[6)] Formaldehyde, which is known as a common indoor pollutant, can also be detected by combining above mentioned SWCNT network sensor and a chemical reaction.[7)] Hydroxylamine hydrochloride reacts with formaldehyde to emit HCl, which injects a hole carrier into semiconducting SWCNTs. The sensor (Fig. 2) can detect trace (0.05 ppm) formaldehyde, and the sensor is reusable. Moreover, the selectivity to formaldehyde is 10^5-10^6 times higher than interferences such as water, methanol, and toluene.

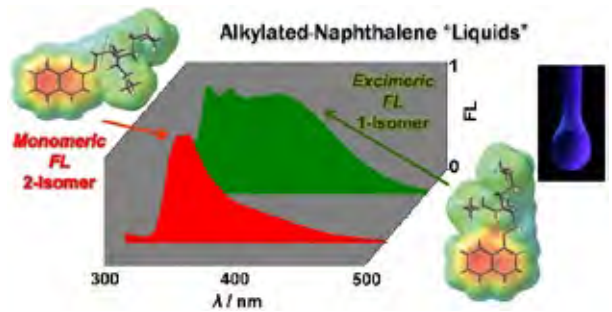

Fig. 1. Novel alkylated naphthalene liquids are presented with a correlation among the 1- and 2- regioisomeric chemical structures, photophysical (monomer or excimer emission), calorimetric and rheological properties.

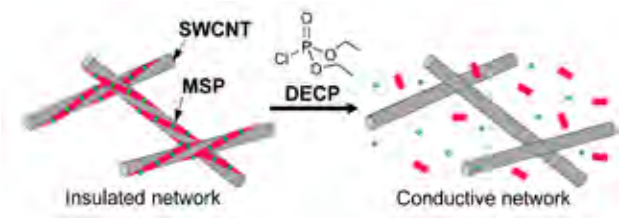

Fig. 2. Schematic illustration of chemiresistive sensor composed of SWCNTs and MSP.

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Semiconductor Devices of Organic Nano-Sheet Crystals

Principal Investigator **Jun TAKEYA**
(The University of Tokyo, Japan)
Cross Appointment with NIMS

1. Outline of Research

It is known that periodically arrayed two-dimensional sheets of molecules can generate diverse functions of cell-biology, regulating communication between inner outer circumstances. Self-assembling nature of the molecules, soft dynamics and large area-to-volume ratio are substantial in such functionalization. In our recent studies of elongated π-conjugated semiconducting molecules, we found that soft nano-sheet single crystal films are self-organized to the size of more than inches and that the electronic device performance is maximized. Moreover, it turned out that the structurally well-defined soft electronic material is highly useful to immediately translate mechanical stimulation to electronic signal, demonstrating a giant strain gauge coefficient exceeding 20.

2. Research Activities

(1) Self-organization of Organic Nano-sheet Crystals.[1,2]

Fig. 1 shows an example of the semiconducting molecules which grows to wafer-scale molecular layer crystals. The molecules of alkylated dinaphthobenzodithiophene (C_n-DNBDT) are first dissolved in organic solvents and are gradually crystallized during evaporation of the solvents at bottom surface of a blade in our home-made equipment with sliding substrate[1] (Fig. 1b). By properly adjusting temperature and speed of the crystal growth, it is found that a-few-monolayer crystal films are reproducibly grown to the size over inches.[2]

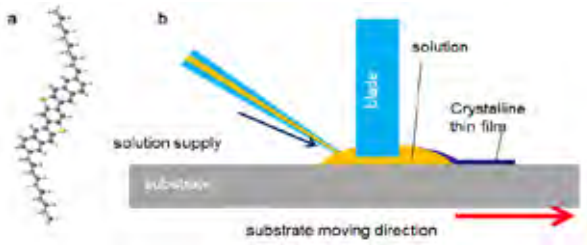

Fig. 1. Molecular structure of Cn-DNBDT (a) and the method of crystallization (b).

(2) Devices of Organic Nano-sheet Crystals.[3]

Bi-layers of the self-organized Cn-DNBDT nano-sheets are grown directly on multilayer substrates of field-effect transistors, presenting outstanding charge transporting property (Fig. 2). The carrier mobility exceeds 20 cm^2/Vs in the transistor channel and the most efficient carrier injection is realized from the top electrodes through the ultrathin film. Therefore, the devices show the fastest response ever realized with molecular semiconductors.[3] With our recent development of high-mobility p- and n-type semiconductor molecules, the result opens the way to printed low-cost CMOS circuits on plastic films. Such organic CMOS technology is highly expected for low-power operation of digital data in battery-less IoT sensors.

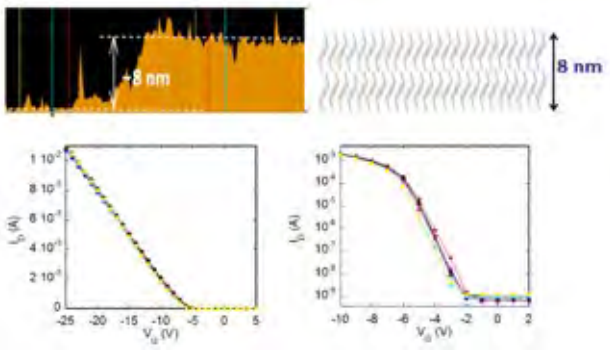

Fig. 2. Bi-molecular-layer Cn-DNBDT semiconductor films and their transistor performances.

(3) Flexible Mechano-electronics.[3,4]

We grew a bi-layer single-crystal film of C_n-DNBDT on a plastic substrate and an acceptor layer is deposited at the top of the nano-sheet crystal film. It turned out that the bi-layer film is efficiently doped with delocalized high-mobility holes because of the minimized thickness of the semiconducting crystal films with negligible defects (Fig. 3). At maximum, 3% strain is uniaxially applied without any damage to the sample so that room-temperature mobility increased by the factor of 1.7.[4] Analysis using X-ray diffraction (XRD) measurements and density functional theory (DFT) calculations reveal the origin to be the suppression of the thermal fluctuation of the individual molecules, which is consistent with temperature dependent measurements.[5]

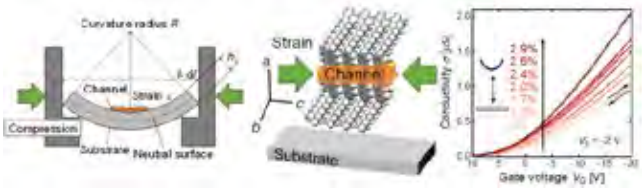

Fig. 3. Giant strain effect in doped nano-sheet organic crystals.

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MANA Satellite | Nano-Materials Field

Light-Triggered Pyroelectric Nanogenerator

Principal Investigator **Zhong Lin WANG**
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X.F. Wang (Graduate Student)

1. Outline of Research

Near-infrared (NIR) light, as electromagnetic radiation with wavelengths between visible and infrared light, has a wide range of applications in biomedical imaging, remote temperature sensing, chemical analyzing, and environmental monitoring. The NIR photo-absorption capacities of emerging materials inherently limit the corresponding performances of the reported NIR photodetectors (PDs). More importantly, fundamentals of these PDs rely on the separation of photogenerated carriers by the built-in electric field formed within pn- and/or Schottky junctions. During this process, photoinduced voltage (PIV) arising from the separated carriers is formed with an opposite direction to the built-in electric field, which can reduce the built-in electric field and weaken the separation of carriers in turn, thus limiting the photoresponse performances of NIR PDs. Therefore, NIR PDs with a rational design are highly required to further improve their performances and expand their practical applications. We demonstrated NIR photothermal triggered pyroelectric nanogenerators based on pn-junctions with a p-Si/n-ZnO nanowire (NW) heterostructure for self-powered NIR photosensing.[1] The pyroelectric- polarization potential (pyro-potential) induced within wurtzite ZnO NWs couples with the built-in electric field of the pn-junction. At the moment of turning on or off the NIR illumination, external current flow is induced by the time-varying internal electric field of the pn-heterostructure, which enables a bias-free operation of the photodetectors (PDs). The NIR PD exhibits a high on/off photocurrent ratio and a fast photoresponse component with a rise time of 15 μs and a fall time of 21 μs. This work provides an unconventional strategy to achieve active NIR sensing, which may find promising applications in biological imaging, optoelectronic communications, and optothermal detections.

2. Research Activities

The p-Si/n-ZnO NW heterostructure devices were fabricated by hydrothermally synthesizing uniform ZnO NWs on a 500-μm-thick Si substrate, as schematically shown in Fig. 1a. Upon the illumination of NIR (1064 nm) from the ZnO side, two optical processes can be induced in the pn-junction device: the instantaneous pyropolarization inside ZnO NWs and the photoexcitation at the local junction caused by the photoabsorption of NIR in 500- μm-thick Si (Fig. 1c). Owing to the existence of E_b within the depletion region of the pn-junction, photogenerated holes and electrons will be separated and driven toward the p-Si and n-ZnO NWs side, respectively (Fig. 1d). The separated charge carriers lead to a photogenerated potential in the opposite direction to E_b. Therefore, the coupling among E_{py},

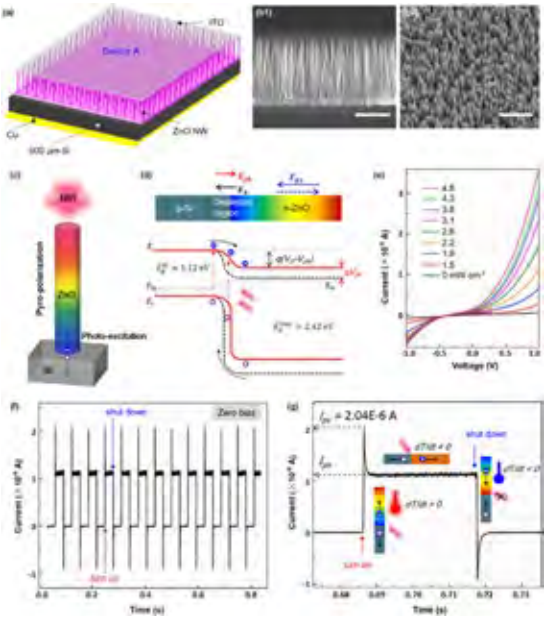

Fig. 1. (a) Schematic image of the 500 μm p-Si/n-ZnO NW heterostructure devices. Cross-section-view (b1) and tilt-top-view (b2) scanning electron microscopy (SEM) images of the as-grown ZnO NWs, both with scale bars of 500 nm. (c) Upon the illumination of 1064 nm light, two optical processesare induced in the pn-junction device: the instantaneous pyro-polarization inside the ZnO NW and the photoexcitation at the local junction. (d) Photogenerated holes and electrons are separated, leading to the generation of Eb. (e) I–V characteristics of the p-Si/n-ZnO NIR PDs under nine different power densities of NIR illumination. (f) Under bias-free conditions, the output-current response of the pn-junction PDs to 4.8 mW cm^{-2} NIR illumination under periodical NIR illumination. (g) One typical cycle of the short-circuit I–t curve.

E_{ph}, and E_b in the heterostructure devices can be expressed by $E_{total} = E_{py} + E_b - E_{ph}$, which dominates the photoresponse behavior and performances of the NIR PDs.

I–V characteristics of the p-Si/n-ZnO heterostructure device under a series of different power densities of NIR light illumination are measured and plotted in Fig. 1e, showing good photoresponse properties of the NIR PDs. Under biasfree conditions, the output-current response of the pn-junction PDs to NIR illumination of 4.8 mW cm^{-2} is systematically investigated and summarized in Fig. 1f by periodically turning on and off the NIR light using an optical chopper. One typical cycle of the short-circuit I–t curve extracted from Fig. 1e is plotted in Fig. 1f. This I_{py} is caused by the time-dependent change of the total electric field inside the pn-junctioned devices due to NIR-photothermal heating induced instantaneous temperature increase ($dT/dt > 0$) in ZnO NWs.

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Chirality Sensing Using Symmetrical Porphyrin Derivatives

Independent Scientist **Jan LABUTA**

1. Outline of Research

Porphyrins are widely studied functional dyes that can complex a great variety of metal cations. In biological systems, porphyrins play essential roles as photosynthetic antenna and reaction centre, in heme proteins as an oxygen carrier, and as vitamin B_{12}. In our research we use porphyrin derivatives for various sensing properties such as enantiopurity sensing, selective detection of anions, determination of trace water impurities in organic solvents or naked-eye discrimination of methanol from ethanol. In the following text, we elaborate the sensing of chirality using symmetrical achiral porphyrin derivatives[1-5] and its potential applications.

2. Research Activities

The two enantiomers of the same molecule act differently when interacting with other chiral species. This is especially important in development of new pharmaceuticals where the the effect depends on identity of enantiomer (e.g. ibuprofen, atropine, etc.). An example of this can be shown as different scent of (*R*)- and (*S*)-carvone. One gives the characteristic smell/taste to spearmint and the other to caraway (Fig. 1). Enantiomeric excess (*ee*) is commonly used as a measure of enantiomeric purity with values ranging from *ee* = 0 % (racemic) to *ee* = 100 % (enantiopure).

Fig. 1. Illustration of different scent of carvone enantiomers.

We have developed novel sensing method utilizing achiral porphyrin derivative **Bz_2OxP**[1,4] (Fig. 2a) in which the chiral information (i.e. *ee*) is translated from chiral analyte to porphyrin (Fig. 2b) and manifests itself as chemical shift nonequivalence of the NMR signals of porphyrin (Fig. 2c). The magnitude of the chemical shift nonequivalence $\Delta\delta$ is always linearly proportional to *ee* (Fig. 2d). **Bz_2OxP** is very versatile detector since it provides acceptable chemical shift nonequivalence for a large variety of differently functional analytes, which is due to interaction of **Bz_2OxP** with the analyte through H-bonding. This system is also of note from the point of view that it does not rely on the formation of diastereomers.[4] This is perhaps counterintuitive given the prevailing opinion that formation of diastereomers is required in the NMR analysis of *ee*.

This novel sensing method has some interesting potential applications.[1,6,7] For example, in situ monitoring of variation of *ee* in enantiomer enrichment or biological processes. This property can be exploited by magnetic resonance imaging

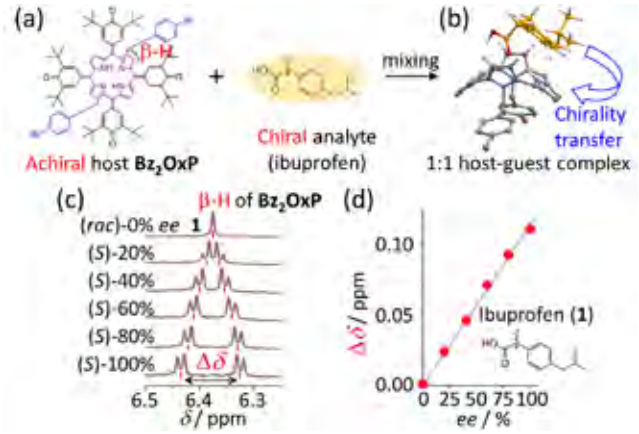

Fig. 2. (a) Structure of achiral porphyrin derivative Bz_2OxP. (b) Transfer of chiral information from analyte to porphyrin. (c) NMR spectra of porphyrin reporting group (β-H) in the presence of various enantiomeric excess (*ee*) of ibuprofen (1). (d) Fundamental linear relationship between induced chemical shift non-equivalency $\Delta\delta$ and *ee* as obtained from (c).

(MRI) for monitoring spatial distribution of *ee* of chiral metabolites in plants, animals or humans (Fig. 3). Some of the commonly used pharmaceuticals, such as ibuprofen or thalidomide, undergo racemization in human body. Thus, originally administered pure enantiomer (with intended effect) will be racemized with different biological effects and metabolism for each enantiomer. *In vivo* monitoring of extend and place of the racemization using MRI remains challenging due to aqueous environment.

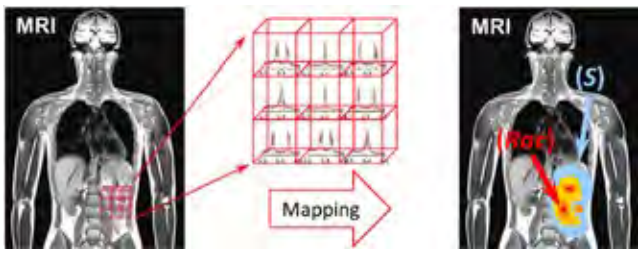

Fig. 3. Schematic visualization of *in vivo* enantiomeric excess (*ee*) mapping of chiral metabolites using MRI.

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GaN Nano-Interface Engineering for Power Electronics Application

Independent Scientist **Liwen SANG**

1. Outline of Research

III-V nitrides semiconductors have much higher breakdown voltages, larger saturation velocity, higher carrier mobility and higher thermal stability compared to the conventional Si or GaAs, which enabled them promising for the high-power and high frequency electronic devices.[1)] The current challenging problems of the GaN power devices are the metal-insulator (oxide)-semiconductor (MI(O)S) interface at GaN and *p*-GaN, which resulted in a threshold voltage instability, large leakage current and low breakdown voltages, hindering their real applications.

In this year, our effort is concentrated on the MIS interface modulation for the GaN and *p*-GaN. A novel two-step surface treatment was proposed for the GaN vertical power devices, and the total trap density was decreased by two orders of magnitude. For the *p*-GaN, we proposed a novel CaF_2 dielectric layer for the MIS capacitors, and successfully suppress the hysteresis in the capacitance-voltage (C-V) performance.

2. Research Activities

(1) Two-step surface treatment for nearly ideal GaN MOS interface.

Although the rapid progress has been achieved in the vertical-type MIS or MOS field effect transistors (FETs), the quality of the MOS interface strongly affects the electrical properties of the devices. The threshold voltage is much lower and the on-resistance is still higher than the expected values due to the insufficient control of the GaN surface potential. To ultimately improve the performance of GaN-on-GaN vertical MOSFETs and realize real applications, a high-quality and stable MIS/MOS interface with low-density trap states not only at the interface but also close to the interface is required. Typically, Al_2O_3 gate insulators are prepared by atomic layer deposition for the GaN MOSFETs. A lot of surface treatments have been attempted to modify the GaN surface, especially GaN films grown on sapphire. Nevertheless, the detailed investigation on the surface modification and their effects on the electrical property have not been performed on the GaN MOS interface with Al_2O_3 insulator especially for the vertical power devices. Moreover, the analysis of different trap states at and close to the interface is lack and different behaviors of trap states have not yet been distinguished.

We proposed a two-step surface treatment including surface cleaning and modification to reduce the trap states of the Al_2O_3/GaN metal-oxide-semiconductor (MOS) interface using epitaxial n-GaN layers grown on the free-standing GaN substrate. The two-step treatments inhibit the formation of disordered regions at the MOS interface, leading to an ultra-low interface state density in the range of 10^{11} $cm^{-2}eV^{1}$. The oxide-trapped charges located at the transition layer between Al_2O_3 and GaN are also suppressed. The improvement of interface morphology can be seen in Fig. 1.

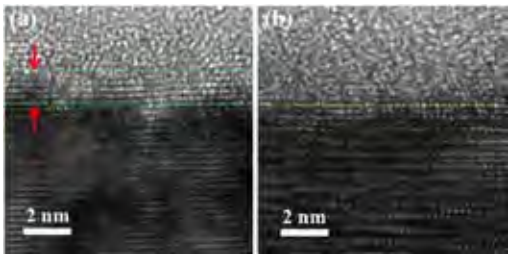

Fig. 1. High-resolution TEM images for ALD-Al_2O_3/GaN interface (a) without any treatment, and (b) with aqueous HF etching + $(NH_4)_2S$ passivation.

(2) Novel dielectric layer for p-GaN MIS capacitors.

We have successfully achieved the first *p*-channel MOSFETs which can be operated from cryogenic temperature to room temperature. It was found that, the quality of the dielectric/*p*-GaN interface is crucial to improve the stability of *p*-channel MOSFETs. Nevertheless, as a result of the Mg accumulation to the surface of *p*-GaN, the typically used ALD-Al_2O_3/*p*-GaN MOS capacitor displayed a serious electrical hysteresis in both the current-voltage and capacitance-voltage properties. The electrical hysteresis could lead to the threshold voltage instability, which is detrimental to MOSFETs.

To ultimately suppress the oxidized trap states, we propose to develop a non-oxide gate dielectric layer-calcium fluoride (CaF_2) with oxygen-free deposition process for the *p*-GaN FETs to improve the quality of the MIS interface. The leakage current of the MIS devices using CaF_2 of just several-nanometer thickness was greatly reduced. Compared to the *p*-GaN MOS capacitor with Al_2O_3 dielectric, the hysteresis in C-V bidirectional sweeping of CaF_2-MIS capacitor is greatly suppressed (Fig. 2). The density of the charged traps is reduced by more than two orders of magnitude, which is due to the suppression of the oxidized transition layer by the oxygen-free dielectric and post annealing process.

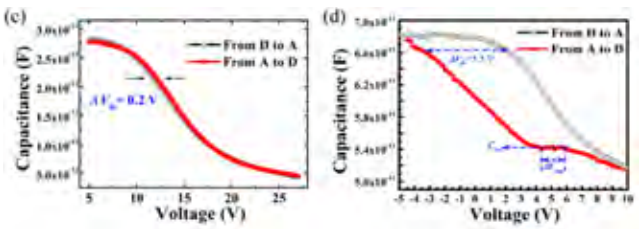

Fig. 2 High-frequency (1MHz) C-V hysteresis plots for the *p*-GaN MIS capacitors with (c) CaF_2 and (d) ALD-Al_2O_3 dielectric layer.

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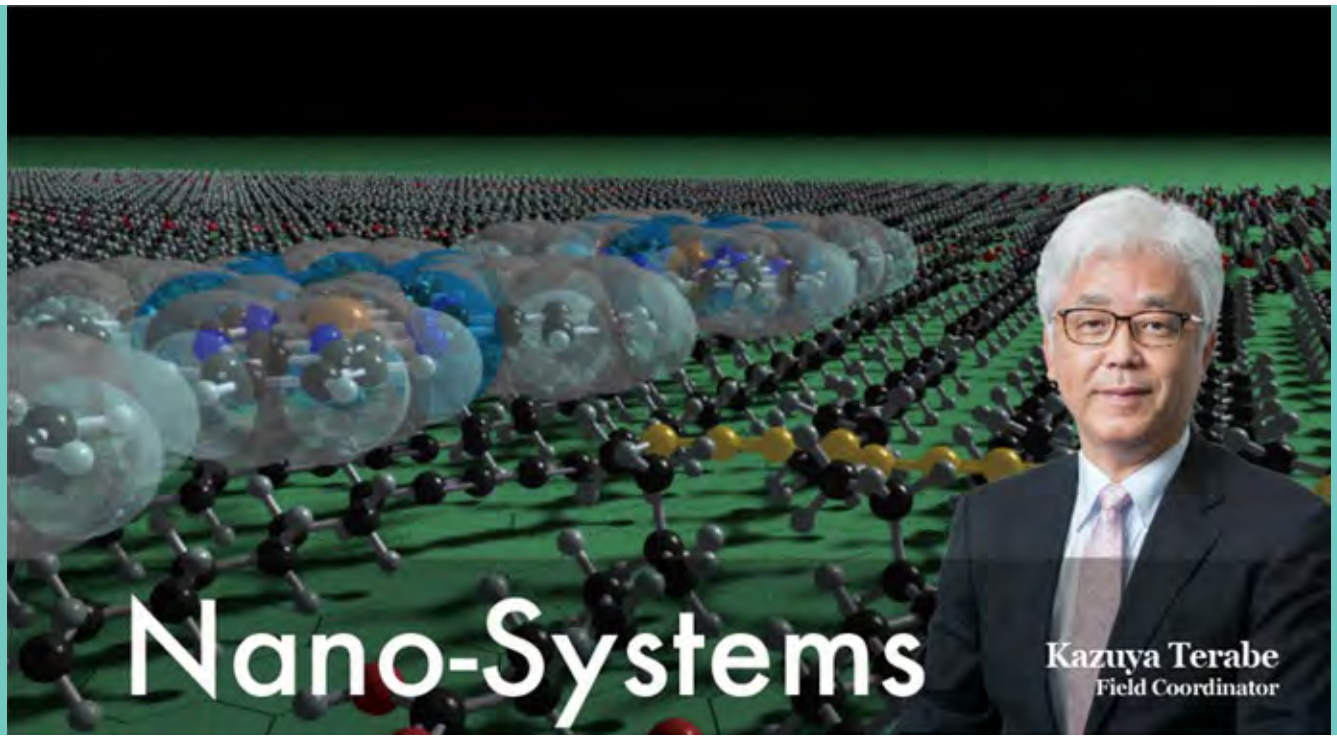

New Nano-Systems are Changing the World: From Artificial Intelligence to Energy and the Environment, Diagnosis and Medicine

This research field is searching for various nano-systems that will express novel functions by the interaction of nanostructures with unique characteristics, and is engaged in research to research to utilize those new nano-systems systematically. Concretely, based on basic research on nanoscale materials, such as atomic and molecular transport and chemical reaction processes, polarization and excitation of charge and spin and superconducting phenomena, we are conducting research on atomic switches, artificial synapses, molecular devices, new quantum bits, neural network-type network circuits, next-generation devices, high sensitivity integrated molecular sensors and other new applied technologies. Since the development of new nanoscale measurement methods is also a high priority, we are developing multi-probe scanning probe microscopes and other cutting-edge instruments. We also attach great importance to interdisciplinary fusion-type research with other research fields in MANA.

Nano-Systems Field
(11 Research Groups)
- Nanoionic Devices Group
- Nano Functionality Integration Group
- Nano-System Theoretical Physics Group
- Photonic Nano-Engineering Group
- Nano Frontier Superconducting Materials Group
- Thin Film Electronics Group
- Medical Soft Matter Group
- Mechanobiology Group
- Surface Quantum Phase Materials Group
- Quantum Device Engineering Group
- Nanomechanical Sensors Group

Nanoionic Devices Group

Nano-Systems Field

Innovative Transistors Based on Magnetically Induced Movement of Ions

Principal Investigator **Kazuya TERABE**
(Field Coordinator, Group Leader)
Yuji Okawa (Chief Researcher), **Makoto Sakurai** (Principal Researcher),
Tohru Tsuruoka (Principal Researcher), **Takashi Tsuchiya** (Senior Researcher)

1. Outline of Research

Electrochemical devices find application in many technologies, including batteries, capacitors, sensors, and atomic switches. For such electrochemical devices to operate, they need an electric field that causes ionic transport and electrochemical processes. This simple but strict rule has long hindered innovation in electrochemistry and related technologies, however, we recently challenged the rule with their development of 'magnetic control of electrochemical devices'.[1)]

2. Research Activities

Fig. 1(a) shows a schematic illustration of the magneto-electrochemical cell (MEC).[1)] Two Au electrodes are placed on the left and right sides of a bottle filled with liquid electrolyte including paramagnetic $FeCl_4$ ion, nonmagnetic [Bmim] ion, and weak diamagnetic H_2O molecule. The electrical properties of the MEC were investigated by attaching or removing small neodymium magnets to switch the magnetic field on and off. The applied magnetic field causes a transport of paramagnetic $FeCl_4$ anion toward Au electrode, resulting in electronic carrier density modulation at the surface of the Au.

Fig. 1(b) shows the variation in the open circuit voltage (OCV) of an MEC with two Au electrodes. Voltage is defined here as E_{left} - E_{right}, where the electrode potentials of the left and right electrodes are E_{left} and E_{right}, respectively.

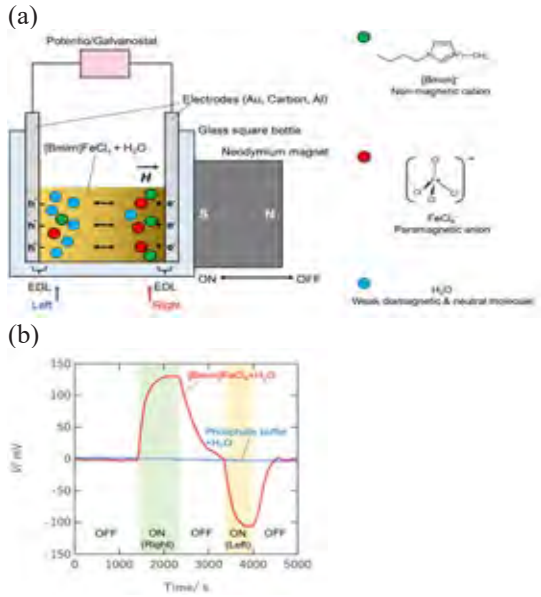

Fig. 1 (a) Illustration of two-terminal MEC and the components. (b) Variation in OCV of the MEC.

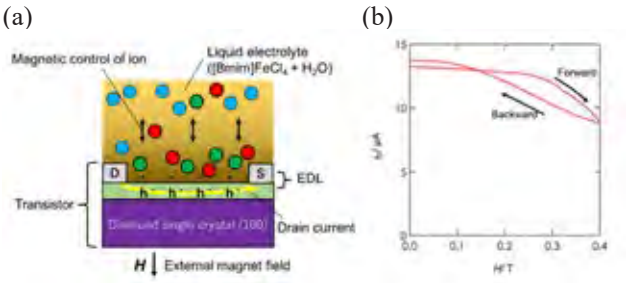

Fig. 2 (a) Illustration of EDLT composed of hydrogen-terminated diamond. (b) Variation in EDLT i_D in response to magnetic field sweep.

When a magnetic field was applied to the MEC from the right side, the OCV immediately started to increase and reached 130 mV. The applied magnetic field drives paramagnetic $FeCl_4$ ion and made the [Bmim]$FeCl_4$ concentration near the right Au electrode much higher than that near the left, causing a significant electromotive force (EMF) between the two electrodes. In other words, the EDLs near the two Au electrodes were differently charged by the magnetic field.

Fig. 2(a) illustrates an electric double layer transistor (EDLT) composed of hydrogen-terminated diamond single crystal (100) and the liquid electrolyte discussed above. The high-quality epitaxial growth with (100) orientation was confirmed by high resolution transmission electron microscopy (not shown). Fig. 2(b) shows the variation in the drain current (i_D) in response to a magnetic field sweep that was applied using an electromagnet from the back side of the device shown in Fig. 2(a). As indicated by the red curve in Fig. 2(b), i_D was reversibly modulated in depression mode (normally on) from 13.6 to 8.8 μA with magnetic field application. The i_D variation (i.e. Magnetoresistance (MR) effect) is attributed to an extrinsic MR effect due to hole concentration modulation by the EDLT mechanism.

MECs and EDLTs containing magnetic electrolyte have been developed. Interfaces and magnetism are two of the few areas that still remain in materials science and physics that have been intensively explored. Deriving useful and novel functions from them is important for dealing with the serious problems in this century (e.g., energy and resource depletion and the information explosion). Our approach should attract researchers toward development of high performance magnetic electrolyte and the combination with electrochemical applications that will lead to novel electrochemical devices.

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Nano Functionality Integration Group

Nano-Systems Field

Integration of Nano Functionality

Principal Investigator **Tomonobu NAKAYAMA**
(MANA Deputy Director, Administrative Director, Group Leader)
Shigeki Kawai (Principal Researcher), **Yoshitaka Shingaya** (Senior Researcher),
Hideo Arakawa ((Principal Engineer)

1. Outline of Research

We develop novel techniques and methodologies toward the realization of novel nanosystems for future information technology. Development and application of advanced scanning probe microscopes such as multiple-probe scanning probe microscopes (MP-SPMs) and fundamental researches on molecular manipulations, low-dimensional nanostructures and neuromorphic networks, are explored. These research contribute to establishing science and technology required for functionalizing nanosystems to transmit, transduce , and even transform electrical, optical, mechanical, ionic and magnetic signals. We are specially interested in spatio-temporal variation of material properties, especially those in nanosystems, because this aspect is an inevitable feature of nanosystems.

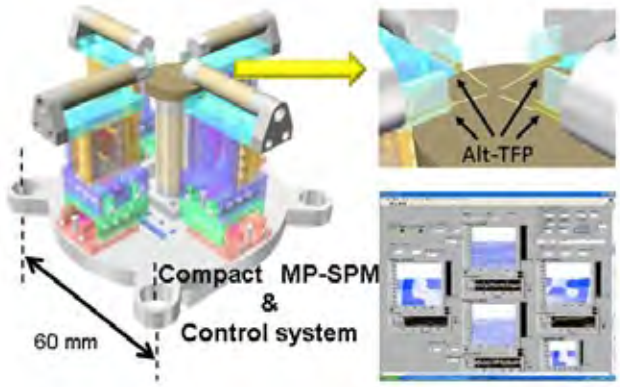

Fig. 1. A new MP-SPM with four Alt-TFP sensors, all controlled from an integrated control system. AFM, KPFM, and other force microscopy modes can be combined in this MP-SPM.

2. Research Activities

(1) Multiple-probe Scanning Probe Microscopes.[1-5]

MP-SPM has simultaneously and independently controlled 2 to 4 scanning probes[1] which are brought into electrical contact to a single nanostructure and reveals its electrical property.[1,2] Implementation of Kelvin-probe force microscopy (KPFM) mode in our MP-SPM realized noncontact observation of potential distribution over a nanosystem under a current bias. As an alternative noncontact MP-SPM operation, eddy-current damping microscopy (ECDM) mode was successfully introduced by detecting eddy-current induced damping of an oscillating magnetic probe, which is useful to obtain a conductance distribution over the nanosystem. The latest MP-SPM (Fig. 1) equips four angled-long-tip tuning fork probe (Alt-TFP) sensors[3] and is operated through the home-built control system. This enables combination of different control modes for each probes.[4] Further improvements regarding spatial resolution of such AFM-based MP-SPM to achieve atomic precision[5] in locating each probe is required.

(2) Fabrication and characterization of functional nanostructures and nanoarchitectonic systems.[6,7]

Creating functional nanostructures and nanomaterials, followed by measurements of their physical properties, is an important part of our research towards a realization of functional nanoarchitectonic systems. In this respect, we are currently working on single-molecule-level ultrahigh density datastorage using thin films of fullerene C_{60} molecules[6] and on neuromorphic networks towards brain-type computing,. Such networks are prepared by assembling functionalized nanowires into the form of entangled complex network.[7]

In the case Ag nanowires (AgNWs), we implemented metal-insulator-metal junctions at each crossing point between two AgNWs. Then, we found interesting switching properties as shown in Fig. 2. It is interesting to point out that the observed switching behavior seem to be cooperative property of massive number of junctions involved in the AgNW network. Further investigation on the AgNW network showed the ON and OFF states respectively exhibit different fluctuation nature in the noise of transmitting electrical current. Also, reproducible long-term and short-term memorization of ON state can be realized by the network, indicating a possibility of a new devices utilizing dynamic noise control.

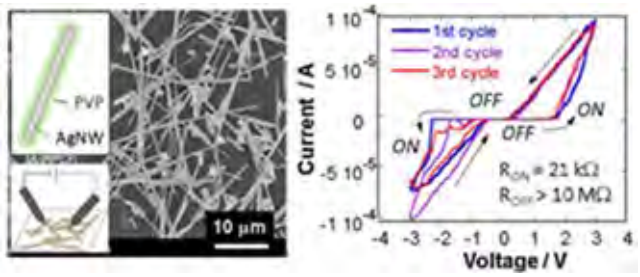

Fig. 2. Chemically prepared Ag nanowires (AgNW) covered with insulating PVP layer were used to form neuromorphic networks.

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Nano-System Theoretical Physics Group — Nano-Systems Field

Topological States in Carbon and Silicon Systems

Principal Investigator **Xiao HU**
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Toshikaze Kariyado (Researcher)
X.C. Sun (Postdoc), Y.C. Jiang (Graduate student), X.X. Wang (Graduate student)

1. Outline of Research

The Nobel Prize in Physics of 2016 was awarded to Thouless, Haldane and Kosterlitz for their pioneering theories on topological phase transition and topological phase of matter. The discovery of quantum Hall effect (QHE) of two-dimensional (2D) electron gas under strong perpendicular magnetic field by von Klitzing opened a new chapter in condensed matter physics. Thouless and his coworkers revealed that the integer coefficient in Hall conductance is given by the Chern number associated with topological phase of electronic wave functions at Landau levels. Afterword, Haldane discovered that nontrivial topology can be created by electronic states with finite Berry curvature defined in momentum space on Bloch electronic wave functions even without external magnetic field. Similar to QHE, the quantum anomalous Hall insulator supports dissipationless edge current. Since then to explore possible topological states in terms properties inherent in materials, such as spin-orbit coupling and/or magnetism has been one of the main driving forces in study of condensed matter physics and related materials science. The concept of topology fostered in electronic systems has been extended to a wealth of systems, and topological superconducting and electromagnetic states have also been explored. It is revealed theoretically that zero-energy Majorana bound states (MBS) at the two ends of 1D topological superconductors and/or vortex centers of 2D topological superconductors obey non-Abelian statistics and can be used for implementing decoherence-free quantum computation. In topological photonic crystals, a unidirectional propagation of electromagnetic wave can be achieved at the sample edge. In terms of an approach coined "topological nanoarchitectonics", we have been exploring novel topological phenomena and quantum functionality derived from topology.

2. Research Activities

(1) Driving graphene topological. [1)]

It is well known that graphene exhibits lineaer dispersions at the corners of Brillouin zone (BZ), known as Dirac cones. It is the origin of excellent physical properties of graphene such as good electric and heat conductivity. In order to make use of graphene in electronic devices, however, one needs to drive graphene into semiconductor in a controllable way. We show that introducing textures in hopping energy between nearest neighboring carbon atoms on honeycomb lattice will open an energy gap in the otherwise Dirac cones as shown in Fig. 1a, 1b and 1c. Moreover, we propose explicitly how to drive the system into a topological phase.

In our approach the texture in hopping energy is characterized by two values t_1 and t_0 with $t_0 = 2.7$ eV, which

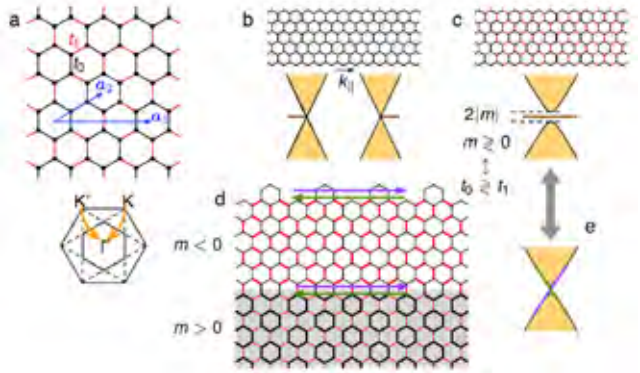

Fig. 1. Strategy to achieve topological transportations in graphene by introducing textures in hopping energy between nearest neighboring sites of honeycomb lattice.

respects the C_{6v} symmetry (see the black hexagonal unit cell in Fig. 1a). The energy gap is given by $m = t_0 - t_1$, which can be either positive or negative depending on the relative values of t_1 and t_0. We clarify theoretically that for $m < 0$ two counterpropagating electronic states appear at the "molecular zigzag" edge of graphene ribbon as shown in Fig. 1d. Similar topology protected currents can be realized at the interface between the domains with $m > 0$ and $m < 0$. These topological properties are related to the mirrow winding numbers, which are evaluated from the electronic bands of graphene with bond modulations.

(2) Optic topological state in fcc lattice of Si spheres. [2)]

Nodal-line (NL) semimetallic states with linear, Dirac-like dispersions over k points on a closed loop in BZ are attracting considerable interests. Because of the nontrivial topology of NLs, almost-flat bands appear at sample surfaces where density of states is enhanced and group velocity is suppressed largely. We reveal that the face-center cubic (fcc) structure hosts NLs due to its rich symmetries, which is termed as "symmetry guaranteed" NL as opposed to other NLs which depend on detail parameters such as interactions among atoms discussed so far in literature. The symmetry-guaranteed NL always passes through the W point in BZ of fcc lattice, which can be taken as its hallmark. The topological NL proposed in our work can be found in elemental solids taking the fcc structure, such as Cu, Ag, Au, In and Ga. Furthermore, we clarify that the fcc lattice of Si spheres exhibits NLs in a frequency window where no other photonic band exists. This provides a unique platform to realize ideal NL under intensive search, and on its own right can be explored for achieving slow lights.

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Photonic Nano-Engineering Group

Nano-Systems Field

Controlling the Infrared Light and Its Energy in Nanospace

Principal Investigator **Tadaaki NAGAO**
(Group Leader)
Satoshi Ishii (Senior Researcher)
T.D. Dao (JSPS Fellow)

1. Outline of Research

Since more than half of the solar radiation is composed of infrared light, harvesting infrared energy from sunlight as well as from thermal radiation associated with industry / human activity has become one of the important approaches towards the sustainable development goals (SDGs).[1] The research on infrared (IR) nanophotonics, the science and technology for regulating the thermal radiation by amplifying, confining, or scattering the IR light with nano-materials has gained significant importance as one of the key technologies for small-scale energy harvesting. Nanophotonic materials, especially plasmonic materials and metamaterials are now accepted as useful paradigms for materials science which enable us to control the light in nanospace with great flexibility. In our laboratory, based on plasmonic/metamaterial approach, we are designing and developing energy-harvesting nano-systems, especially for highly-efficient photothermal applications and wavelength selective IR light emission and detection.[2,3] Along with the device fabrications, we also explore various types of plasmonic compounds with appropriate optical properties, suitable for the high-temperature applications, efficient photothermal conversion, hot carrier generation, as well as high surface electromagnetic field enhancement.[4]

2. Research Activities

(1) Arbitrary wavelength selectivity in mid-IR with simple 1D structures.

Wavelength-selective IR ligh sources are strongly required for the application in nondispersive IR gas sensing as well as in drying furnaces for lithium battery fabrication. Such light sources realize low-power-consumption IR gas sensors, as well as cool and fast drying of solvents with high flammability. So far, complex 2D or 3D nanostrucutres have been commonly seen in nanophotonics resreaches and wavelength selective structures are no exeptions. However, 1D structure, yet simple, can offer novel photonic properties that cannot be found in natural materials. In the current work, we demonstrate wavelength selectivity in mid-IR with 1D structures[2] (Fig. 1). The structure consists of periodic dielectric multilayers which work as distributed Bragg reflector and a metal layer. At the interface of the periodic structure and the metal, surface waves are excited depending on the design and materials. After the analytical electromagnetic calculations, we fabricated the sample by supperting technique and showed wavelength selective absorption in mid-IR. When the same sample was heated, it emitted narrow thermal emissions. 1D structure has advantage in fabricating large samples for thermophotovoltaic and mid-IR heaters.

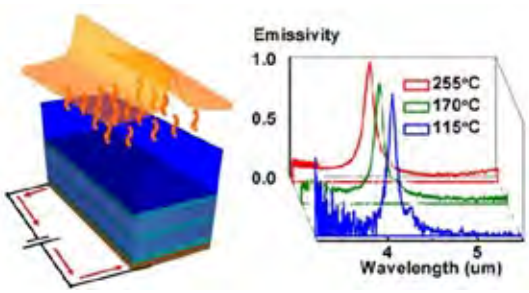

Fig. 1. Schematic diagram of 1D mid-IR perfect absorber based thermal emitter (left) and its thermal emissivity in experiment (right).

(2) High-resolution spectroscopic mid-IR detector array.

Engineering light absorption at desired wavelengths using nanophotonic structures enables a wide variety of applications which do not exist in nature. In the past decades, plasmon-enhanced light absorptions for enhancing energy conversion efficiency have attracted many attentions owing to their potential applications in solar energy harvesting, light emitting devices, and infrared and heat transfer devices. In this work, we demonstrate an IR sensor array in which each resonant sensor exhibits four-wavelength detection with sub-100 nm wavelength resolution[3] (Fig. 2). To realize high wavelength resolution as well as making them industry compatible, the structural design has been intended to efficiently absorb the thermal radiation at desired wavelengths with narrow window using Si nanofabrication techniques. The developed four-wavelength-selective IR sensor array exhibits a high performance with sub-100 nm bandwidth responsivity, which can be applied for non-dispersive IR spectroscopy, multicolor IR imaging, and remote sensing of absolute temperature.

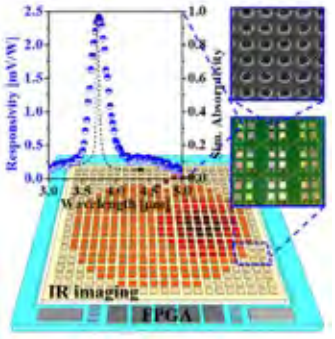

Fig. 2. (Bottom) A schematic diagram of a multicolor (four-wavelength-selective) IR imaging device. (Top-right) An SEM image of the fabricated four-wavelength-selective IR sensing chips array. (Top-left) Typical spectrum from a single IR detector with IR resonance designed at 3.7 μm, showing a narrowband responsivity.

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Nano Frontier Superconducting Materials Group Nano-Systems Field

Insulator-Metal-Superconductor Transition in SnSe Induced by Diamond Anvil Cell with Metallic Diamond

Principal Investigator **Yoshihiko TAKANO**
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Hiroyuki Takeya (Chief Researcher)
R. Matsumoto (JSPS Fellow)

1. Outline of Research

High pressure is a promising tool to obtain new functional materials which cannot appear under ambient pressure. For example, the discovery with great surprise of high-transition temperature superconductivity in H_3S at 203 K was recently reported under 150 GPa. Diamond anvil cell (DAC) is most useful apparatus to generate high pressures, however, the resistivity measurement using DAC is quite difficult because it requires a small sample size (< 100 μm) and hard electrodes. Moreover, an insulating layer should be inserted between the electrodes and a metal gasket, which is also broken by applying pressure. In this study, we focused on the boron-doped metallic diamond and undoped diamond as a very hard electrode and an insulating layer, respectively.[1,2)]

2. Research Activities

The diamond electrodes and insulating layer were fabricated on the bottom diamond anvil using electron beam lithography and a chemical vapor deposition method. Fig. 1 shows (a) the schematic of our new DAC assembly, and (b) optical microscope image of diamond electrodes and insulating layer. The transport property such as the resistivity and the Hall coefficient can be measured by using five proves of electrodes. Moreover, an electric double-layer transistor can be formed on the diamond anvil using V_g prove. If two proves of electrodes are used as a heater, high temperature synthesis of material and/or high temperature in-situ X-ray structural analysis can be performed under high pressure. These functions are quite useful for wide fields of material science.

We performed the electrical transport measurement of SnSe with remarkable thermoelectric performance, using our new DAC. This material is also expected as a candidate high-temperature superconductor because it has flat band

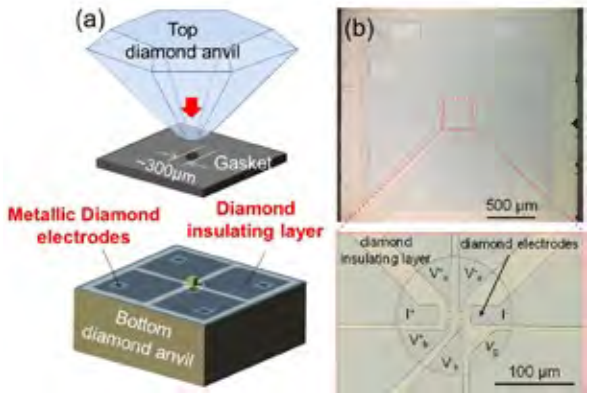

Fig. 1. (a) Schematic of new DAC, (b) optical microscope images of diamond electrodes and insulating layer.

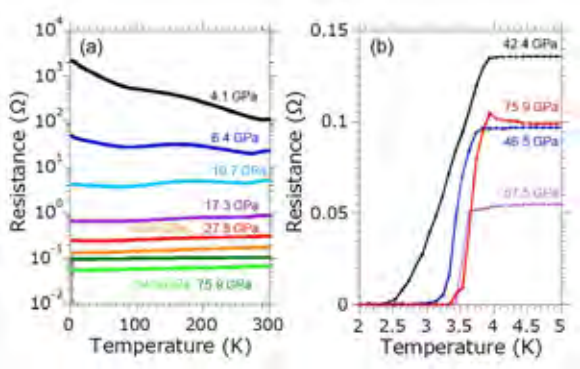

Fig. 2. (a) Temperature dependence of resistance in $SnSe_{0.99}S_{0.01}$ under pressure, (b) enlargement of superconducting transition.

near the Fermi energy. Fig. 2(a) shows temperature dependence of resistance in hole-doped $SnSe_{0.99}S_{0.01}$ under various pressures. The sample shows semiconducting behavior below 10.7 GPa, however, it changed to metallic above 17.3 GPa. When the pressure increased up to 42.4 GPa, a sharp drop of resistance corresponding to superconductivity was clearly observed around 4 K as shown in Fig. 2(b). With increase of pressure, superconducting transition temperature increases, and shows the maximum value of T_c^{onset} ~4.3 K, T_c^{zero} ~3.4 K at 57.5 GPa. Fig. 3 shows a phase diagram of hole-doped $SnSe_{0.99}S_{0.01}$ up to 75.9 GPa. By using our new DAC, we have successfully observed pressure induced insulator-metal-superconductor transition in hole-doped $SnSe_{0.99}S_{0.01}$. The superconductivity still survives at least 75.9 GPa. As shown in these results, the pressure can induce drastic changes of the physical properties.

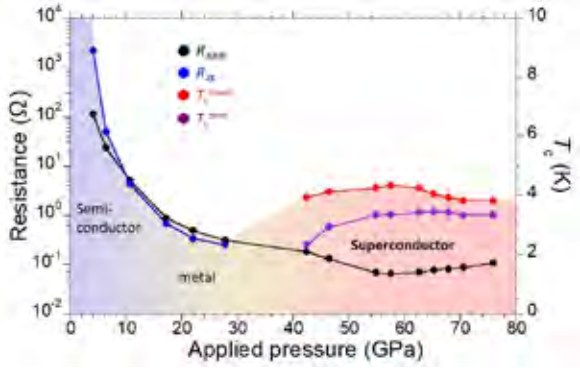

Fig. 3. Phase diagram of hole-doped $SnSe_{0.99}S_{0.01}$ single crystal.

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Thin Film Electronics Group

Nano-Systems Field

Hetero-Double Layer InSiO Thin Film Transistor

Principal Investigator **Kazuhito TSUKAGOSHI**
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Seiichi Kato (Senior Researcher)
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1. Outline of Research

As for pixel swithing thin film transistor (TFT) in the flat panel display, amorphous silicon or poly-silicon film has been customerily used. But because of serious large off-state current in the current TFTs, a new TFT is strongly desired to realize a low-power consumption system. Furthermore, higher mobility of TFT than the amorphous silicon is needed to present high resolution contents for next generation high-quality display. Amorphous metal oxide thin-film transistor (a-OxTFT) is a possible candidate as the post silicon TFTs. Although the InGaZnO film is one of the candidates of the a-OxTFT, however, the InGaZnO is unstable film in actual production. This is because the electric property of the film is a very sensitive to oxygen absorption or desorption at the bonding sites adjacent to Zn atoms.[1)]

2. Research Activities

Here, we discovered that the electric stability of the TFT is determined by the bond-dissociation energy of the dopant element in InOx film (Fig. 1). By incorporating the dopant with higher bond-dissociation energy, such as Silicon atom, the film supresses thermal active vacancy in the film. The basic property of our original InSiO-OxTFT has exceeded that of current commercial production TFTs.

Furthermore, we developped homogeneous double-layer amorphous InSiO-OxTFT with an insulating ISO cap layer on top of a semiconducting ISO bottom channel layer

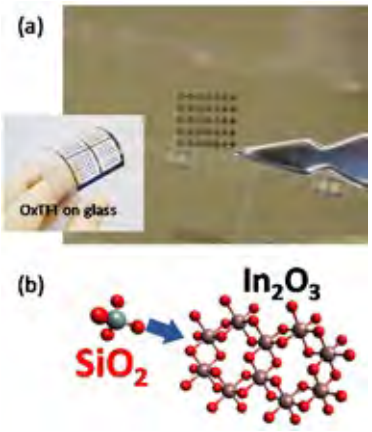

Fig. 1. (a) **Photo images of stable amorphous In_2O_3-based thin-film transistors by incorporating SiO_2 fabricated on glass substrate. (b) Schematic of vacancy suppression in In_2O_3 by incorporating SiO_2.**

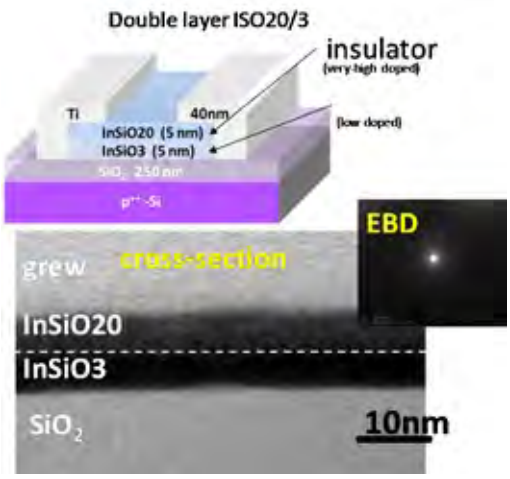

Fig. 2. Cross-sectional TEM image of the double-layer films with vertically stacked ISO20 and ISO3 on a SiO_2/Si substrate. The inset shows an electron-beam selected-area-diffraction (SAD) image.

(Fig. 2). The homogeneously stacked ISO TFT exhibited high mobility (20 cm^2/Vs) and normally-off characteristics after annealing in air. It exhibited normally-off characteristics because the ISO insulator suppressed oxygen desorption, which suppressed the formation of oxygen vacancies (V_O) in the semiconducting ISO. In the double-layer amorphous InSiO-OxTFT, we investigated the recovery of the double-layer ISO TFT, after a large negative shift in turn-on voltage caused by hydrogen annealing, by treating it with annealing in ozone. The recovery in turn-on voltage indicates that the dense V_O in the semiconducting ISO can be partially filled through the insulator ISO. Controlling molecule penetration in the homogeneous double layer is useful for adjusting the properties of TFTs in advanced oxide electronics.[2)]

Our recent challenging development of InSiO-TFT utilizing atomic layer deposition method has pushed up further high-performance ISO-TFT. Then, the developed material for oxide thin film transistor will realize a very stable and high-performance TFT with highly suppressed off-state current to produce a next generation power-saving flat display.

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Medical Soft Matter Group

Nano-Systems Field

Biomedical Application of Phospholipid Particles

Group Leader **Kohsaku KAWAKAMI**

Chiho Kataoka (Senior Researcher), **Yoko Shirai** (Principal Engineer)

1. Outline of Research

Phospholipid is one of the most useful materials as pharmaceutical excipients because of many advantages including high bio-compatibility and easiness of chemical modification. It is now used as a constituent of the representative drug carrier, liposome. However, liposome exhibited excellent performance only as an injectable carrier, and it does not function well for solid dosage forms. We have developed phospholipidic solid mesoporous particle, which may be used as a novel platform carrier for drug delivery[1] (Fig. 1). Production of mesoporous phospholipid particle (MPP) is very simple. In the preparation, hydrogenated soybean phosphatidylcholine (HSPC) is dissolved in a mixture of cyclohexane and t-butyl alcohol (BuOH) at 50 °C, followed by incubation of the solutions below the liquid-liquid demixing temperature to induce precipitation, which is obtained in a spherical morphology because of microphase separation. The precipitates were subsequently freeze-dried leading to formation of a mesoporous structure in the particles. MPP can accommodate both hydrophilic and hydrophobic drugs, and may be used for various administration routes including oral, injectable, nasal, and pulmonary delivery.

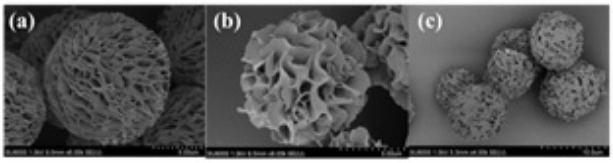

Fig. 1. SEM (Scanning electron microscopy) images of MPPs. (a) HSPC MPP prepared from cyclohexane/t-BuOH solution. (b) HSPC MPP prepared from cyclohexane/t-BuOH/water solution. (c) HSPC/FEN = 9/1 MPP.

2. Research Activities

As one of the application examples, use of MPP as a drug carrier for oral delivery of poorly soluble drug[2] is introduced below. Fig. 1(c) shows MPP, which was prepared with fenofibrate (FEN), a poorly soluble drug. Although porous structure was lost, the spherical structure was maintained. In the dissolution tests, FEN was not released from MPP in buffered media; however, prompt release was observed when a small amount of surfactant was added. It was because of formation of mixed micelles composed of surfactant and HSPC. Initial size of MPP was larger than 10 μm, and it decreased to ca. 1.2 μm after 4-h incubation in the presence of 0.1% Tween 80. Sodium taurocholate (TCNa) was more effective for the size reduction, achieving a particle size of ca. 220 nm. In comparison, the HSPC liposome was subjected to the same study to find that it was much more stable relative to MPP against the surfactants. Tween 80 did not influence its particle size during the incubation. Although size reduction was achieved in the presence of TCNa, the resultant particle had a diameter of ca. 1.3 μm, which obviously showed that MPP was much more reactive to surfactants compared to liposomes. This is presumably due to the highly hydrophilic surface of liposomes, which are protected by a hydrated water layer; this should not the case for MPP, which was prepared by freeze-drying in the organic solvent. The resultant small particle should be crude mixed micelles composed of HSPC and the surfactant. In the animal studies, this HSPC/FEN MPP improved oral absorption of FEN compared to crystalline FEN. The property of MPP to easily form smaller particles can advantageous for improving the absorption of poorly absorbable drugs via an oral route as schematically represented in Fig. 2.

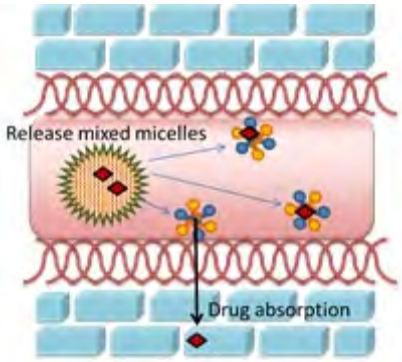

Fig. 2. Mechanism of drug absorption from MPP.

MPP may be used for any administration routes except intravenous injection where size of the carrier must be smaller than the MPP by more than an order of magnitude. The most promising application may be as a carrier for dry powder inhalation. Typically, aerodynamic diameter of MPP is 1-2 μm, which is suitable for pulmonary drug delivery since effective deposition deep in the lung is expected. Further modification of the characteristics such as particle size, pore structure, and surface property should widen its potential as a novel drug delivery platform.

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Mechanobiology Group

Nano-Systems Field

Materials for Cellular Mechanobiology

Group Leader **Jun NAKANISHI**

Mitsuhiro Ebara (Associate PI), **Takeshi Ueki** (Senior Researcher), **Chiaki Yoshikawa** (Senior Researcher)

1. Outline of Research

Mechanobiology is a discipline that studies the role of physical force in life phenomena. Recent studies in this field shed light on the significance of force, comparable to chemical and biochemical cues, in the regulation of various biological and pathological processes. We are developing new materials and methodologies, based on the concept of nanoarchitectonics, not only to study basic principle in mechanobiology,[1,2] but also to develop drug screening platforms and medical devices.[3,4]

2. Research Activities

(1) Sparse adhesive ligand induces leader cell appearance by changing the balance between cellular mechanical force and cell-cell cohesion.[5]

Leader cells, appeared at the front edge of collectively migrating epithelial cells have an important role in the determination of the directionality and speed of the following cell clusters. Therefore, it is important to understand how the environmental cues affect the population as well as activity of leader cells. In contrast to the impact of soluble factors and gene expression, that of extracellular matrices (ECMs) is still controversial, because most studies utilize substrates with physically-adsorbed ECM proteins, which are amenable to protein remodeling. We used a photoactivatable substrate to study the impact of an ECM-derived cyclic Arg-Gly-Asp (cRGD) ligand on leader cell formation (Fig. 1A, B). This robust platform allowed us to investigate the effect of cRGD density on leader cell formation with minimized ECM remodeling (Fig. 1C). Our results show the increased appearance of leader cells on reduced levels of the surface ECM ligand. Moreover, this increase is not only associated with the weakening of

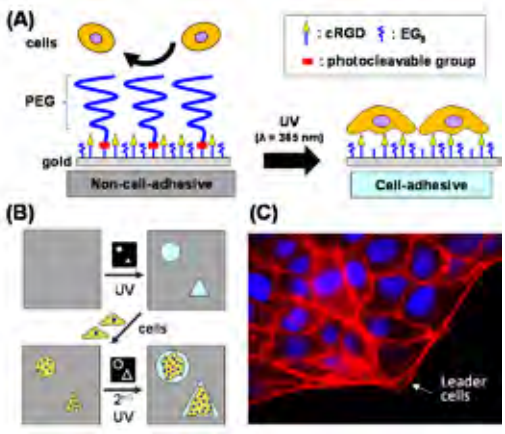

Fig. 1. Study of leader cells by using photoactivatable substrates.

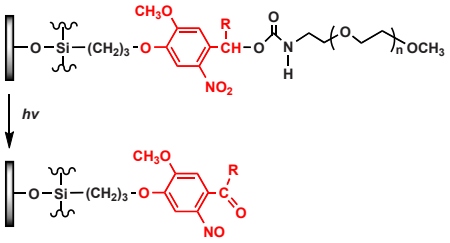

Fig. 2. Chemical structure of new photoactivatable interface.

circumferential actomyosin belts, but also reduction of cellular traction and intercellular junctional E-cadherin. These results indicate that cRGD-mediated cell-ECM interactions positively regulate mechanical and biochemical coupling within cell clusters; both are critical for the coordination of cell collectives and eventual reduction in the appearance of leader cells (Fig. 1D).

(2) Photoresponsive interfaces bearing 2-nitrobenzyl ester with a bulky substituent.[6]

Photoreponsive dynamic materials are useful platforms for studying cellular mechanobiology in high spatiotemporal resolutions. One of the most commonly used "photoswitches" for such purpose is the 2-nitrobenzyl ester, which cleaves upon absorption of near-UV light. The temporal resolution of the dynamicity of such materials inevitably depends on the kinetics of the photocleavage reaction. However, most studies in this direction stick to conventional 2-nitrobenzyl ester. We developed photoactivatable substrates based on 2-nitrobenzyl ester derivatives with a bulky substituent (Fig. 2). The new substrate exhibited complete switching from non-cell-adhesive to cell-adhesive state with approximately one-fifth shorter irradiation time than the conventional photoactivatable substrate. Moreover, the UV dose needed for the full conversion of the conventional substrate caused reactive oxygen species production, whereas there was no apparent deleterious effect for that needed for the new substrate. These results clearly indicate the advantage of the new bulky benzyl derivative compound for the development of dynamic culture materials based on 2-nitrobenzy ester.

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Exploring Surface Atomic-Layer Superconductors with Advanced Nanotechnology and Instrumentation

Group Leader **Takashi UCHIHASHI**

Ryuichi Arafune (Senior Researcher), **Katsumi Nagaoka** (Senior Researcher), **Takahide Yamaguchi** (Senior Researcher)

1. Outline of Research

Recent advancement in nanotechnology has led to realization of two-dimensional (2D) superconductors with truly atomic-scale thicknesses.[1] Since this is against the general belief that 2D superconductivity cannot exist or should be at least very fragile, the finding is surprising and has attracted much attention. Particularly, we successfully demonstrated the existence of ideal 2D superconductivity, by growing epitaxial indium atomic layers on a silicon surface and by directly measuring macroscopic superconducting currents for the first time.[2] This surface atomic-layer superconductor was found to have a very high critical current density, and in addition, includes natural Josephson junctions at atomic steps. These features are preferable in terms of its potential use as a component of superconducting electronic devices.

The uniqueness of the surface atomic-layer superconductors lies in the fact that they are exposed to the surface and interface. This can result in two important effects. First, their superconductivity can be sensitive to a surface overlayer or the underlying substrate because their total thickness is of atomic scale and is comparable to the Coulomb screening length. This means that a charge transfer through the surface/interface may strongly influence the superconducting properties of the whole system. Second, the space-inversion symmetry, which is held for most of bulk materials, is lost because of inequality of the vacuum and substrate sides relative to the surface atomic layer. If the material has a strong spin-orbit interaction, this naturally leads to the Rashba effect and a spin-split Fermi surface. Since superconductivity is driven by the instability of electrons near the Fermi level, the Rashba effect can have strong influences on superconductivity. In our group, we are working on these two effects through our advanced experimental techniques.

2. Research Activities

For a 2D superconductor, we used indium atomic layers on silicon, which is technically called the Si(111)-($\sqrt{7}\times\sqrt{3}$)-In surface. For the organic molecules, phthalocyanines with Cu and Mn atoms coordinated at center were used (MPc, M = Mn, Cu). They were found to form nearly identical well-ordered molecular monolayer, which were commensurate with the underlying indium atomic layer. This hybrid system is considered a derivative form of the van der Waals heterostructure. Unexpectedly, our electron transport measurements revealed that the monolayers of MnPc and CuPc had opposite effects on the superconducting transition temperature (Tc); the Tc shift was negative for MnPc but positive for CuPc. Namely, superconductivity is suppressed by MnPc while it is enhanced by CuPc. This distinctive behavior was attributed to a competition of charge and spin effects, based on the results of X-ray magnetic circular dichroism (XMCD) measurements and *ab initio* calculations. Particularly, the directionality of the *d*-orbitals of Mn and Cu atoms was found to play a decisive role.[3]

We are also studying the superconductivity of the indium atomic layers at very low temperatures and under strong magnetic fields using a newly developed instrument. A fully ultrahigh-vacuum (UHV) compatible cryostat has been constructed where four-terminal electron transport measurements can be conducted at sample temperatures as low as 400 mK and under magnetic fields as high as 5 T (Fig. 1). Samples prepared in other UHV instruments can be transferred to this machine without exposing them to air using a portable UHV chamber. Surprisingly, their superconductivity was found to be highly robust when a magnetic field was applied to the sample in an in-plane direction. The in-plane critical field extrapolated toward zero temperature was 15-20 T, which was 3-4 times larger than the Pauli limit field of $H_P = 5.6$ T, which corresponds to $T_c = 3$ K. This intriguing phenomenon can be attributed to the Rashba effect of the system. In our group, we are also working on observation of Rashba effect-induced spin-polarized photocurrents, fabrication of high-mobility diamond FET devices, and STM characterization of single molecule devices. In the future, these studies will be fused and combined for the development of novel atomic-layer materials with useful device functions.

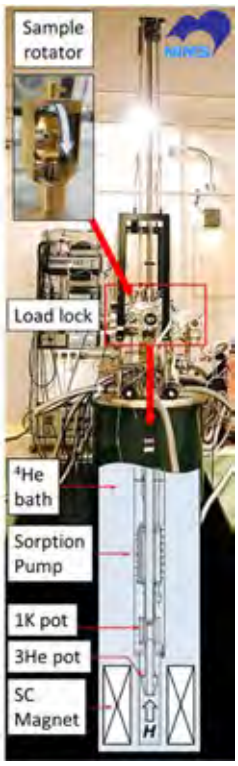

Fig. 1. Photograph and schematic illustration of the newly developed UHV-compatible cryostat. A sample can be loaded through the top load-lock chamber without breaking vacuum. The instrument accommodates superconducting magnet.

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Quantum Device Engineering Group

Nano-Systems Field

Multi-Functional Electron Tunneling Devices with Molecular Quantum Dots

Group Leader **Yutaka WAKAYAMA**

Shu Nakaharai (Principal Researcher), **Ryoma Hayakawa** (Senior Researcher), **Satoshi Moriyama** (Senior Researcher)

1. Outline of Research

Tunneling transistor has attracted attention as a potential candidate for low power consumption and highly-integrated devices since a few decades ago. However, this device still has not reached practical application. This is because that it is necessary to produce quantum dots precisely, which are the key component in tunneling transistors. In spite of recent progress in micro-fabrication technologies, to control the quantum dot size of 10 nm or less is still a difficult challenge even today. A main purpose of our research is to solve this problem by taking advantages of organic molecules as quantum dots because the size and structure can be controlled and, therefore, electronic states of the molecules can be also precisely designed.

Until now, we have investigated electron tunneling behaviors through organic molecule and reported a variety of functional tunneling phenomenon, including basic mechanism,[1] multi-level tunneling by multiple molecules[2] and optical controllability of tunneling.[3] Based on these studies, we report the latest progress, where multi-step switching was achieved in a vertically aligned tunneling transistor.

2. Research Activities

In general, quantum dots in tunneling devices should be well designed on nanometer scale for realizing stable and reproducible operation at room temperature. To meet these requirements, we adopted organic molecules as quantum dots. In this study, C_{60} molecules were embedded in a double-tunneling junction consisting of $Au/Al_2O_3/C_{60}/SiO_2$ multiple layers on highly-doped Si substrates.

First, we examined a fundamental mechanism of the tunneling carrier transport. Staircases were observed in current-voltage curves in the two-terminal device configuration. We elucidated that the observed stepwise electrical current can be attributed to a resonant tunneling through the empty and occupied energy levels of the C_{60} molecules. Energy-level diagram to explain this mechanism is illustrated in Fig. 1(a).

Second, we applied this mechanism to develop a tunneling transistor. Vertically-aligned tunneling transistors were fabricated by electron lithographic techniques. A schematic illustration and a cross-sectional TEM image are shown in Fig. 1(b) and 1(c), respectively. In this device, the highly-doped Si substrate works as a source electrode and gate bias voltage can be applied from a side gate electrode.

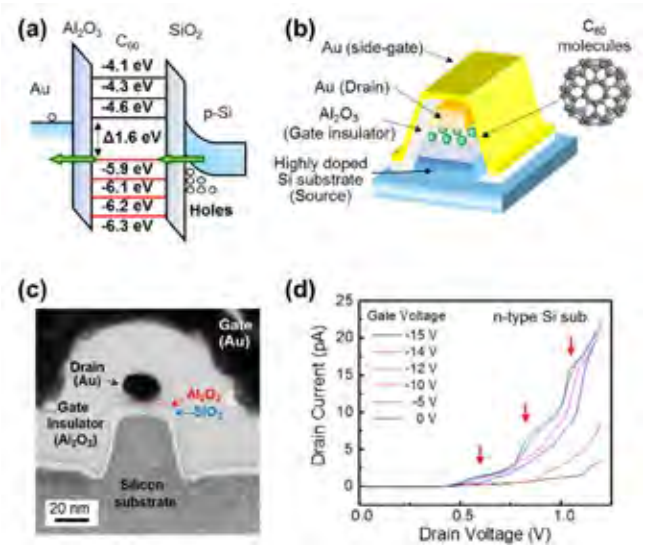

Fig. 1. (a) Energy-level diagram of a double-tunneling junction consisting of $Au/Al_2O_3/C_{60}/SiO_2/Si$ multi-layers. Holes are resonantly tunneling from a p-Si to Au electrode through occupied molecular orbitals. (b) Illustration and (c) cross-sectional TEM image of vertical tunneling transistor. (d) I_d-V_d curves under various gate bias voltage, showing multi-step switching (see red arrows).

Both electrons and holes were resonantly transported through molecular orbitals, which were observed as staircases in drain current-drain voltage curves. More importantly, the observed staircases were modulated by gate bias voltage. Drain current-drain voltage curves measured under various gate voltages are shown in Fig. 1(d). Careful analyses revealed that applying side-gate voltages produced depletion layers in Si substrates, to achieve effective modulation of the drain current. These experiment results demonstrate that the molecule-based tunneling transistor allows multi-level switching through discrete energy levels of molecular orbitals. This is the first demonstration of single-molecule-originated electric properties realized in a Si-based device, meaning that conventional fine processing technologies are applicable to molecular electronic devices, which enable high speed and low power operation, and large-scale integration.[4]

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Nanomechanical Sensors Group

Nano-Systems Field

Nanomechanical Sensors with AI Towards Olfactory IoT Sensing Systems

Group Leader **Genki YOSHIKAWA**

Kota Shiba (Researcher)

1. Outline of Research

Demands for new sensors to detect or identify target molecules are rapidly growing in various fields, such as food, agriculture, medicine, security, and environment science. Nanomechanical sensors have potential to contribute to these global demands owing to their intrinsic versatility. Based on the recently developed platform "Membrane-type Surface stress Sensor (MSS)",[1] we are now trying to realize useful nanomechanical sensor systems which can fulfill the practical requirements, such as portability, low-cost, ease of use, in addition to the basic specifications, e.g. high sensitivity and selectivity.

2. Research Activities

(1) Development of functional receptor materials/layers.[2]

Nanomechanical sensors detect the mechanical stress induced by the adsorption of gaseous molecules on a receptor layer. While the stress is generated as a result of multiple physical/chemical phenomena, the larger surface area usually enhances the signal intensity because of a larger number of adsorbed molecules. We demonstrated such signal enhancement with functional receptor layers based on highly networked capsular silica−porphyrin hybrid nanostructures.[2] As shown in Fig. 1, the larger surface area leads to the larger signal, achieving sub-ppm level detection of acetone vapors.

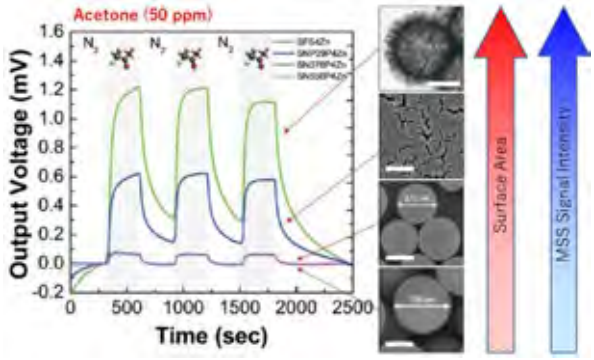

Fig. 1. Sensing signals of MSS coated with Zn porphyrin-functionalized solid silica particles with various diameters. SEM scale bar: 250 nm.

(2) Data-driven nanomechanical sensing.[3]

Odors are known to be composed of thousands of chemicals with various concentrations, and thus, the extraction of specific information from such a complex system is still challenging. Through the combination of MSS with functional nanoparticles and machine learning technique, we demonstrated the specific information extraction; alcohol content quantification as a proof-of-concept, from the odors of liquors. Kernel ridge regression was used to predict the alcohol content of the samples,

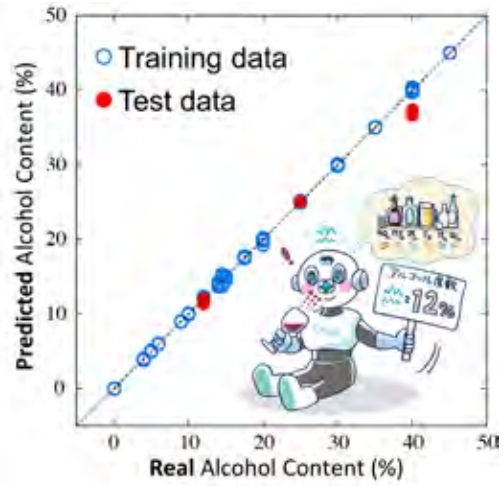

Fig. 2. Parity plot of predicted alcohol content versus real alcohol content under an ambient condition.

resulting in successful alcohol content quantification. Moreover, the present approach provided a guideline to improve the quantification accuracy; hydrophobic coating materials worked more effectively than hydrophilic ones. Based on the guideline, we experimentally demonstrated that additional materials, such as hydrophobic polymers, led to much better prediction accuracy as shown in Fig. 2. The applicability of this data-driven nanomechanical sensing is not limited to the alcohol content quantification but to various fields including food, security, environment, and medicine.

To establish a *de facto* standard for odor analysis and sensor systems employing the MSS technology, the "MSS Alliance" (Fig. 3) was launched in 2015 jointly with companies and a university. Based on the successful demonstrations of various applications utilizing comprehensive olfactory sensor technologies developed in the MSS Alliance, the "MSS Forum"[4] was launched on November 1st, 2017 to encourage interested companies to perform demonstration experiments.

Fig. 3. The MSS logo.

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Materials for Functional Nanomedicine

Managing Researcher **Hisatoshi KOBAYASHI**

1. Outline of Research

In general, organism selected quite limited molecules such as amino acids, lipids, sugar moieties, and limited metals and inorganics, and combined the limited molecules and finally constructed such highly functionalized complex systems. From the structure point of view, the organism is constructed by various nano-fibers and nano-particles under the highly dimensionally controlled condition. We mimic this system to create highly functional biomaterials for several applications.

2. Research Activities

(1) Reepithelialization and remodeling of decellularized corneal matrix in a corneal epithelial wound model.

This study aims to investigate the correlation between re-epithelialization and re-modeling of the decellularized corneal matrix prepared by high-hydrostatic pressure (HHP) method in vivo. The decellularized corneal matrices were transplanted in a 6mm diameter recipient corneal interlamellar pocket with a 2 to 4 mm epithelial window (Fig. 1). The time course of graft status was examined daily for 6 months by biomicroscopy and scored for clarity and reepithelialization, after which animals were sacrificed for histological analysis. Fluorescein staining revealed that the corneal epithelial cells were migrated onto the decellularized corneal matrix. Histological analysis revealed that the implanted decellularized corneal matrix was completely integrated with the recipient rabbit cornea and the stratified corneal epithelia consist of multiple layers were regenerated on them, which was similar to the native cornea. The recipient keratocytes infiltrated into the decellularized corneal matrix at 6 months after the operation and the decellularized corneal matrix was gradually remodeled to recipient tissue. Transmission electron microscopy (TEM) observation revealed that the ultra-structure of decellularized corneal matrix was re-arranged, which was equal to native corneal ultra-structure. These findings suggested that the decellularized corneal matrix serve as a template for remodeling. The decellularized corneal matrix obtained through HHP is useful graft for corneal tissue regeneration.

(2) Comparison study of endothelial adhesion on no-aged surface of the various PCI Drug eluting stents in vitro.

Drug-eluting stent system is evolving toward achieving the long term tissue compatibility to improve the polymeric component used as strut as well as the materials for controlling drug delivery. As the means to achieve the hemo-compatibility of the device, in the initial stage early endothelialization on the surface is one of the key factors.

In this study, we aimed to compare the endothelial adhesion on the samples. Seven different stents which have been already sold in worldwide markets were evaluated. Sample A and B are fully coated with durable PVDF-HFP polymer include an immunosuppressive, anti-cancer drug (Everolimus) on the strut. Sample C is fully coated durable polymer (BioLinx) with drug (Zotarolimus) on the strut. Sample D is fully coated with biodegradable PLLA include drug (Sirolimus). Sample E is made by SUS-316 stainless steel with abluminal coating with drug (Biolimus) without any polymer. Sample F is made by Co-Cr alloy with abluminal coating with Poly (*d-l* lactide co-caprolactone) include drug (Sirolimus). Sample G is made by Pt-Cr alloy with abluminal coating with PLGA include drug (Everolimus).

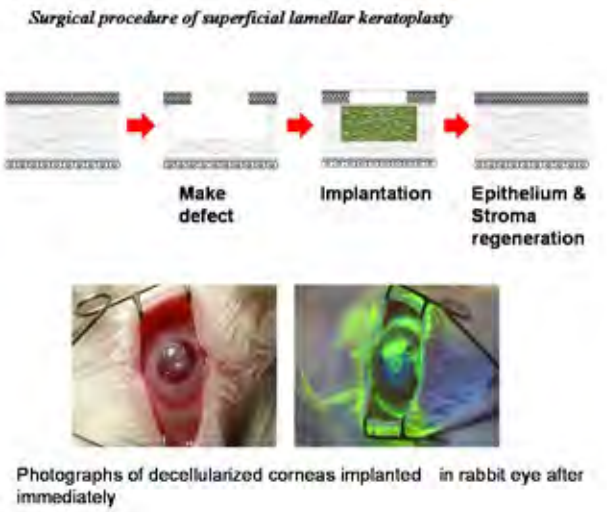

Fig. 1. Surgical procedure and outlook of implanted decellularized porcine cornea in rabbit cornea

In this experiment, we just added endothelial cells suspension from the top and cells were randomly access the surface of the stent strut. Adhered cell numbers were counted from the pictures that were randomly taken the five different places on luminal surface of the stent strut by using image J 1.51j8 software.[1)] Even in the condition, notable tendency were recognized. In case of sample E, adhered cells number dramatically decreased after four day culture. Sample E is specially designed as polymer-free for drug elution. In this case, drug bursting release was happened and the drug caused the endothelial cell damage during the culture. Bear metal surface, especially Pt-Cr alloy surface, is much better substrate for endothelial cells adhesion in initial stage. Polymer carrier for the drug is important to control the drug eluting speed. And aged sample results will be discussed to compare to this non-aged results.

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MANA Satellite | Nano-Systems Field

Neuroarchitectonic Atomic Switch Networks

Principal Investigator **James K. GIMZEWSKI**
(MANA Satellite at UCLA, USA)
Adam Z. Stieg (Satellite Vice Director)

1. Outline of Research

Transformational advances in computation are needed to address ever-increasing societal demands for the collection, processing, and analysis of large, unstructured, multisensory datasets. Conventional computing hardware is excellent at performing deterministic tasks involving error-free calculations, but it faces fundamental constraints in more complex applications such as autonomous control, pattern recognition, or prediction. In contrast, natural systems autonomously process information in complex environments with extreme energetic efficiency.

General purpose computing architectures must therefore be re-defined to consider dynamic and adaptive systems that process information in novel and scalable ways. Through a convergence of nanoarchitectonics, neuroscience, and machine learning, we have developed hardware-adaptive computing architectures known as Atomic Switch Networks (ASN) based on deeply hierarchical networks of nanoscale circuit elements.[1)] This research strives to realize revolutionary efficiency, performance and robustness in real-time, high-performance computing applications.

2. Research Activities

Spatiotemporal dynamics inherent to natural systems are associated with an intrinsic capacity for computation, where the spontaneous emergence of complex behavior occurs through the collective interaction of non-linear elements. Emulating the computational performance of natural systems requires new materials, architectures, and conceptual frameworks in which the development of functional nanomaterials integrating memory and information processing capabilities will support breakthroughs in the design and application of next-generation, neurocomputing systems.

ASN devices utilize the intrinsic memory capacity and adaptive interactions of atomic switches to generate a class of emergent operational characteristics[2,3)] which can be readily applied to real-time information processing and computational tasks.[4)] The unique characteristics of the ASN as a purpose-built complex adaptive system for next-generation computing are the result of its self-organized structure and intrinsic dynamical nature. As seen in Fig. 1, ASN devices comprise individual atomic switch elements embedded within a network of highly-interconnected, self-organized nanowires integrated into a CMOS compatible device platform.

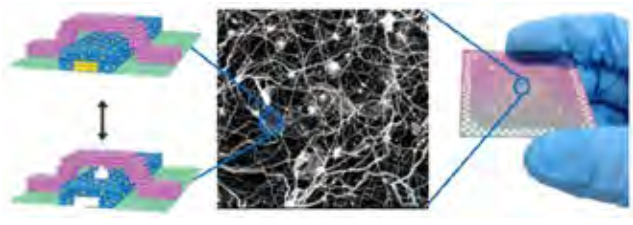

Fig. 1. Multi-scale schematic of the ASN device architecture.

(1) Self-organized nanosystems.

ASN devices consist of highly interconnected, physically recurrent networks of inorganic atomic switches fabricated through simple electrochemical processes. ASN devices comprise up to 10^9 individual atomic switches per cm^2, each of which provides short- and long-term memory based on its history of prior stimulation. These networks form the basis of a device platform fabricated through conventional microfabrication. This merger of bottom-up and top-down fabrication provides a device architecture compatible with CMOS microelectronics for heterogeneous computing applications.

(2) Nonlinear network dynamics.

Switching events at individual atomic switch interfaces distributed throughout the network produce a non-linear current-voltage response. Interactions amongst atomic switches, facilitated by the recurrently connected network of silver nanowires, produce additional emergent, system-wide behaviors including: 1/f noise, temporal metastability, and persistent conductance fluctuations correlated in space and time.[3)] When stimulated, the ASN produces a constantly reconfiguring potential landscape due to the intrinsic volatility of its constituent elements. The resultant nonlinear transformation of input signals throughout the network underlies the ASNs potential for computing applications based on complex adaptive systems.[4,5)]

(3) Intrinsic Computing.

Intrinsic computing utilizes the physiochemical properties of a material system to integrate and process information. The dynamical nature of the ASN has been effectively utilized to successfully implement a series of real-time computational tasks[1)] including waveform generation, t-maze, parity-n, logic, and chaotic time series prediction. These results embolden future efforts to develop adaptive computing systems as a means to produce environmental impacts brought on by reduced energy consumption and socioeconomic benefits built upon increased access to actionable information.

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MANA Satellite | Nano-Systems Field

Surface Atomic Scale Logic Gate

Principal Investigator **Christian JOACHIM**
(MANA Satellite at CNRS, France)
C. Durand (Assistant Professor), W.H. Soe, (Senior Researcher),
O. Faizy (Postdoc), S. Srivastava (Postdoc)

1. Outline of Research

The Pico-Lab CEMES-CNRS Toulouse MANA satellite is working on the experimental and theory of QHC logic gates, their current intensity read-outs, their mechanical inputs and on the exploration of the atomic scale logic gate complexity roadmap to master the emergence of a quantum computing power inside a single molecule or at the surface of a passivated semi-conductor.

2. Research Activities

(1) Preparing the LT-UHV 4-STM for the 1st nanocar race.

After the announcement of the 1st international nanocar race beginning of 2013, it took us 3 years to transform the Toulouse LT-UHV 4-STM in an instrument able to be controlled at the same time by 4 different drivers independently and on the same surface. We have designed and constructed a unique UHV sublimation masking system to sublimate the 4 very different selected molecule-cars on 4 different locations of the shared Au(111) surface.[1] Such unique experimental configuration and its reconfigured software is now ready for atomic scale 4 STM transport measures with a positioning precision better than 10 pm and a 0.8 pA tunneling current closed feedback loop functioning limit for each of the 4 tips independently.

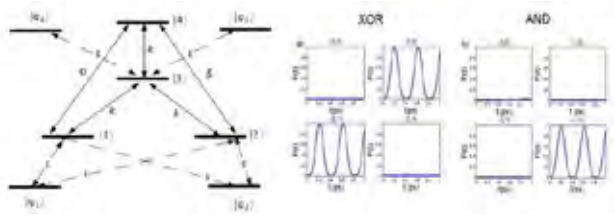

Fig. 1. ½ adder graph on the {|φa>, |φb>, |1>, |2>, |3>, |4>, |φc>, |φd>} canonical basis. The calculating block is defined on the {|1>, |2>, |3>, |4>} subspace, the 2 reading heads on {|φa>, |φb>} and {|φc>, |φd>}, respectively. (α, β) are the classical logical inputs.

(2) Design of complex QHC logic gates.

We have designed a QHC 1/2 adder with a minimum of 4 quantum where the 3 qubits are normally required in quantum computing. Two quantum states encode the digital inputs and two are used to measure separately the AND and XOR outputs i.e. the level repulsion effect. It results a 4 x 4 matrix Hamiltonian (Quantum graph, Fig. 1). For the 2 outputs, the mathematics behind QHC is also requiring that the coordinates of the 4 eigenvectors be optimized on the Fig. 1 canonical basis set for an exact ½ adder functioning (Fig. 1). The corresponding molecules are now under design (Fig. 2).

(3) A planar nanographene molecule ½ adder.

The Fig. 2 nanographene molecule is the smallest ever designed ½ adder Boolean logic gate including its nitro chemical group inputs and the 4 graphene nanopads for the read-out. Having both the calculating board and its measuring nanopads made of the same materials insures the largest possible output current intensities for the XOR and the AND outputs.[2]

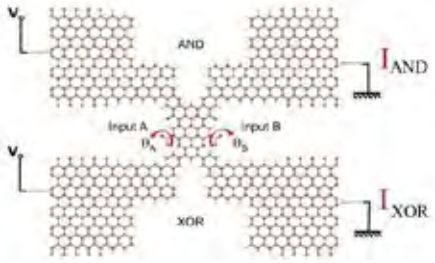

Fig. 2. The molecular design of a QHC ½ adder with its central nanographene calculating unit and the 4 graphene nanopads.

(4) The nanocar race (28-29 April 2017).

The nanocar race was hosted at the Toulouse CNRS MANA Satellite with 6 teams from all over the world. Four teams drove their nanocars on the CEMES LT-UHV 4-STM and shared the same gold surface. The 2 other remote-controlled from Toulouse a single tip STM in their own lab. At 11:00 am on the 28th of April 2017, the departure flag was raised in the control room (Fig. 3). At 5:00 pm the following day and after two days and one night of intense efforts, two teams were ranked equal first: Rice–Graz and Basel.

Rice–Graz successfully drove over a very long 1 µm run in 29 hours on their silver surface, a new kind of world record for the nanoscale. Basel drove for 133 nm on the shared gold surface, crossing the finishing line in 6.5 hours. Ohio was declared third and Dresden fourth. Tsukuba was not ranked and was awarded the 'fair play' prize.[3] The Toulouse team was not ranked because they push mechanically their molecule-car (it was against the nanocar race rules).

Fig. 3. The control room with the 6 teams during the nanocar race.

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MANA Satellite | Nano-Systems Field

Nanoarchitectonics Applied to Interfaces for Studies in Mechanobiology and the Design of Biomaterials

Principal Investigator **Françoise M. WINNIK**
(MANA Satellite at UdeM, Canada)
B. Qi, J. Niskanen, G. Beaune (Postdoc)

1. Outline of Research

Our research aims to address current challenges in mechanobiology and tissue engineering through physical and chemical surface design and fabrication, cell biology, and theory.

2. Research Activities

(1) Sulfobetaine-substituted chitosan substrates.metastasis.

Zwitterionic moieties, such as phosphorylcholine (PC) and sulfobetaines (SB), possess a cation and an anion linked to the same monomer residue. Interfaces coated with zwitterions possess outstanding non-fouling characteristics. They are used increasingly to replace PEG as stealth materials against the adsorption of proteins and cells *in vitro* and *in vivo*.[1)]

We prepared SB-substituted chitosans (0.20 to 0.40 mol SB/mol of glucosamine residues). We evaluated their non-fouling characteristics and mechanical properties by quartz crystal microbalance with dissipation (QCM-D) and surface plasmon resonance (SPR). Suitable SB-chitosan substrates were subjected to *in vitro* assays using cellular aggregates, or spheroids, consisting of hundreds to thousands of cohesive cells. Spheroids are used increasingly as tumor models in biophysical studies,[2)] in drug testing, and in toxicity studies, in preference to 2D cell cultures, as they are more representative of *in vivo* situations.

The spreading of cellular aggregates (CT-26 murine colon carcinoma cells) on chitosan and SB-chitosan substrates was evaluated by bright field optical microscopy (Fig. 1). When cellular aggregates are deposited on a chitosan surface, isolated cells escape from it, and migrate away in its periphery. In the case of SB-chitosan substrates, cellular escape from aggregates diminishes severely with increasing SB content. This phenomenon is attributed to the decrease in cell/substrate adhesion and to the enhanced softness of the substrates as their SB content increases. This characteristic of SB-chitosans suggests their use in evaluations of the ability of cells to undergo the epithelial to mesenchymal transition observed in cancer metastasis.[3)]

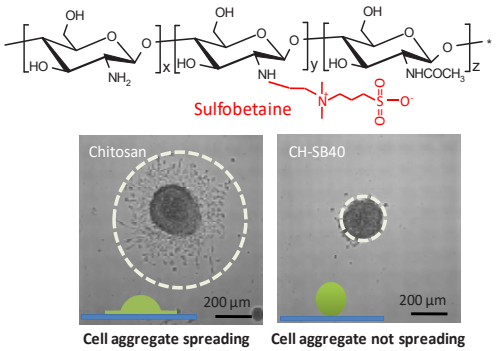

Fig. 1. Schematic view of cellular aggregate spreading on substrate coated with chitosan and CH-SB40 films.[3)] The cell aggregate spreads on chitosan films, but not on CH-SB40 films.

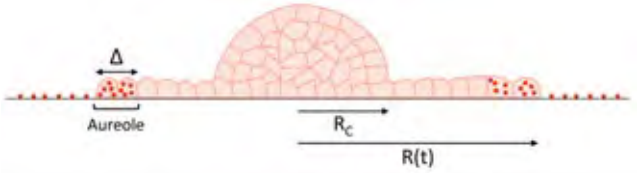

Fig. 2. Schematic view of an aggregate spreading on a substrate coated with particles.[4)] The precursor film is a cell monolayer. Cells on the film periphery digest the particles, forming an aureole of cells full of particles.

(2) Cellular aggregates and particles.

In collaboration with F. Brochard-Wyart of the Institute Curie (Paris, France), we study the spreading of cell aggregates deposited on adhesive substrates decorated with particles. In the case of microparticles (MPs), cell monolayer expands around the aggregate. The cells on the periphery of the monolayer take up the MPs, clearing the substrate as they progress, and forming an aureole of cells filled with MPs (Fig. 2). We monitored the dynamics of spreading and determined the width of the aureole and the level of MP internalization in cells as a function of MP size, composition, and density. From the radius and width of the aureole, we quantified the volume fraction of MPs within the cell.[4)] This method is an easy, fast, and inexpensive assay of the level of particle internalization in cells. The clearing of particles by cells also plays a role in wound healing, where macrophages and leucocytes clean wounds by eliminating dead cells and bacteria. It also bears similarities with the phenomenon of autophagy, the self-eating of cells.

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Signal Analysis for Chemical Sensor Systems

Independent Scientist **Gaku IMAMURA**

1. Outline of Research

Olfaction is the only human sense that has not been fully reproduced as a practical sensor. As olfaction plays an important role in our daily lives, artificial olfaction is expected to be applied to various fields such as food, medicine, environment, cosmetics, and safety. To realize an artificial olfactory system, not only sensing units (*i.e.* chemical sensor arrays) but also signal analysis is essential in the identification of smells. For more valid and reliable identification, I develop signal analysis methods for gas sensing systems by means of data-driven science. I also investigate the sensing signals on the basis of the working principle of the sensors for scientifically-sound identification protocols.[1,2)]

2. Research Activities

(1) Transfer Function.

In the conventional gas sensing approach, the strict control of the entire measurement system is required because each component (flow rate, flow path, pump, *etc*.) in the system affects the output signal. To overcome this issue, I developed a novel identification approach based on transfer function, with which such a strict control is no longer needed. A gas sensing system can be regarded as a conversion process, the relationship between the inputs (*i.e.* sample gas flow) and the output signals is determined as the transfer function. Since the transfer function is determined solely by the interaction between the sensor and a gas, it is not affected by any measurement condition. Therefore, this new approach based on the transfer function realizes the gas identification regardless of any sampling condition. Based on transfer function, I measured smells of herbs and spices using membrane-type surface stress sensor (MSS) and developed a machine learning model for identifying the smells. Even though the sample gases were injected randomly, I successfully identified the smells at an accuracy of 0.94±0.04 (Fig. 1).

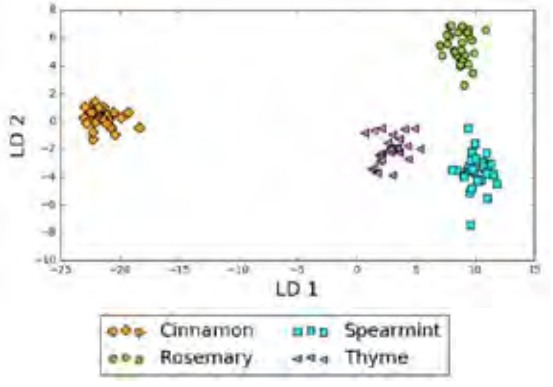

Fig. 1. The LDA scatter plot of the dataset of transfer functions for herbs and spices.

(2) Theoretical Model for Nanomechanical Sensors.

A nanomechanical sensor is a chemical sensor that detects changes in mechanical properties caused by gas sorption (*e.g.* deflection, stress, and mass). Thus, the transient response of nanomechanical sensors reflects various interactions between sensing materials and sample gases, enabling one to extract scientific parameters. In this study, I developed theoretical models for the transient response of a cantilever-type sensor coated with a viscoelastic material. These models allow us to extract several intrinsic parameters including the time constant for gas diffusion τ_s, which reflects the physicochemical interaction between a gas species and a receptor material. On the basis of τ_s extracted from different receptor materials, I succeeded in the identification of the solvent vapors. This new analysis approach utilizing a physicochemical index provides not only a new gas identification protocol based on the intrinsic property of target gases, but also a scientific guideline for the selection and optimization of receptor materials (Fig. 2).

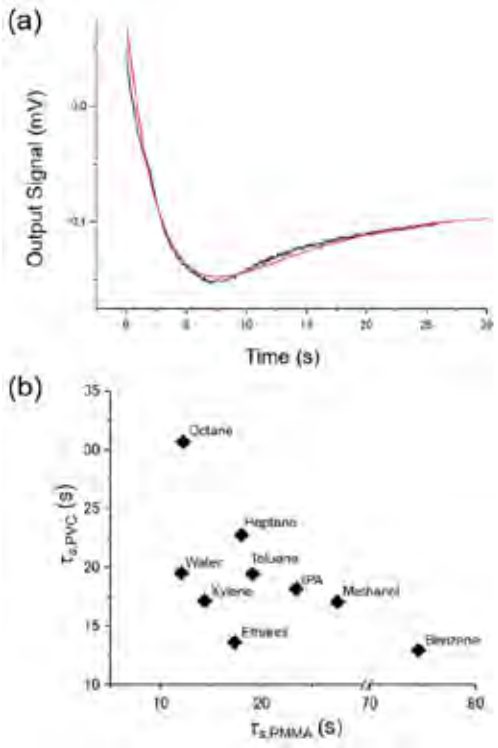

Fig. 2. (a) A sensing signal of the MSS (black line) and the fitting curve based on the theoretical model (red line). (b) A 2D plot of τs extracted from two different polymers.

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Magnetic Property of Organic Dirac Fermion System

Independent Scientist **Takako KONOIKE**

1. Outline of Research

Since the discovery of graphene, it has been attracting a great deal of interest because the electrons in graphene behave like massless Dirac fermions. In contrast with normal electrons with parabolic energy band structure, Dirac fermions show anomalous behaviors resulting from the peculiar liner dispersion, so-called Dirac cone. It is now become evident that such a linear dispersion is realized not only in graphene, but also in various materials. In particular, organic conductor is known to be a first bulk crystal of Dirac fermion system. By taking advantage of its bulk nature, we experimentally study the physical properties of Dirac fermions in this organic compound.[1,2)]

2. Research Activities

Organic conductor α-(BEDT-TTF)$_2$I$_3$ is composed of organic molecule BEDT-TTF and inorganic anions I$_3$. These molecules are stacked alternatively and forming a multi-layered structure of conducting and insulating layer, respectively. At ambient pressure, this compound is semi-metallic and undergoes semimetal-insulator transition at 135 K accompanied by charge ordering. By pressurizing the sample above 15 kbar, the charge ordering state is suppressed and then the Dirac cone dispersion appears in the energy band structure.

(1) Orbital diamagnetism in Dirac fermion system.

The anomalously large diamagnetism in bismuth has been clarified that the orbital diamagnetism due to the inter-band effects of magnetic field plays an essential role in Dirac fermion systems.[3)] Theoretically, graphene is also expected to show a large orbital diamagnetism in low temperature,[4)] though the clean single crystal is too small to detect the intrinsic nature of massless Dirac fermions. Here, we study the magnetic properties in organic Dirac fermion system.

(2) Magnetic susceptibility of Organic Dirac fermion system.

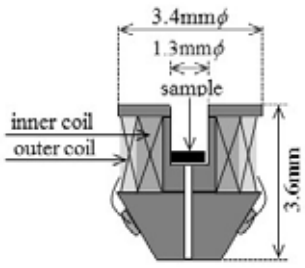

Fig. 1. Pickup coil.

The magnetic properties of organic conductor under pressure are generally investigated by using SQUID magnetometer. However, this method needs large amount of samples to detect the sample signal superimposed on large background from the pressure cell. Here, we tried to apply the field modulation technique to measure the ac susceptibility of one piece of single crystal.

Fig. 1 shows the pickup coil for ac susceptibility measurements. The dimensions of the coil are determined by the sample space in the pressure cell. The pickup coil consists of inner and outer coils. These coils are wound inversely, and the number of turns is adjusted not to detect the electromotive force induced by the uniform modulation field and external magnetic field sweep. Single crystal sample is set into this coil as shown in Fig. 1. These are capped by a Teflon capsule filled with a pressure transmitting medium and then set to the clamp type pressure cell. The measurements were performed in a dilution refrigerator and superconducting magnet. The external magnetic field is modulated by a small ac field generated by the field modulation coil. As a reference, we measured the ac susceptibility of graphite at ambient pressure, and successfully detected clear quantum oscillations (de Haas-van Alphen oscillations) by using this system (Fig. 2). It shows that high sensitive measurement is achieved. Then, we measured the magnetic susceptibility of α-(BEDT-TTF)$_2$I$_3$ at 15 kbar. We observed the temperature-dependent signal at low field regions. However, it is confirmed that most signals originate from the piston in the pressure cell, because it comes close to the pickup coil as the pressure increases. We will change the piston material and improvement of the design of pressure cell is now in progress.

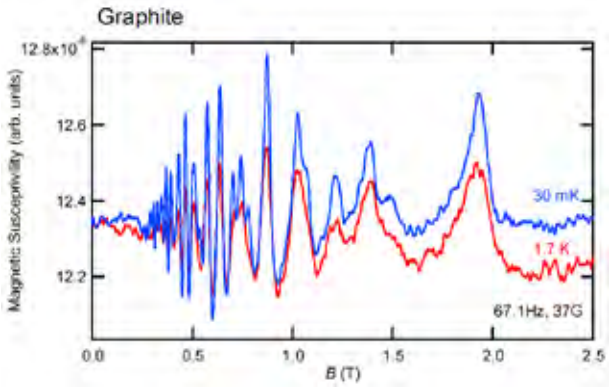

Fig. 2. Magnetic susceptibility of graphite at 0 kbar.

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Printable Electronic Devices with Nano Materials

Independent Scientist **Takeo MINARI**

1. Outline of Research

Fabrication of electronic devices by solution-processed printing is now attracted considerable attentions due to the low-temperature processing and low cost.[1-3] We have developed printable electronic devices using soluble nanomaterials such as metal nanoparticles, organic semiconductors and polymers. Here we present high-performance organic thin-film transistors and memories fabricated by fully-printing techniques.

2. Research Activities

(1) Fabrication of high-performance organic thin-film transistors by printing.

Unidirectional dewetting enables the production of large-area thin films in high efficiency at low cost. Here we developed the simple method to control the unidirectional dewetting on large-area microdroplet arrays (MDAs), which was induced via the gravity-induced deformation in droplets combined with alternating lyophilic/lyophobic patterns (Fig. 1).[4] The MDAs were prepared by surface wettability contrast guided by a printed lyophobic polymer layer including wettable bank regions. It was found that increase of substrate tilted angle enabled the deformation of droplets, thus leading to the homogeneous receding of upper TPC lines from top to bottom on the MDAs. The unidirectional dewetting allowed the deposition of highly-crystalline discrete organic semiconducting thin films in large area, which can be applied for fabrication of fully-printed OTFT arrays. The resulting fully-printed OTFTs exhibited the field-effect mobility of 13.1 $cm^2 V^{-1} cm^{-1}$ for C_8-BTBT.

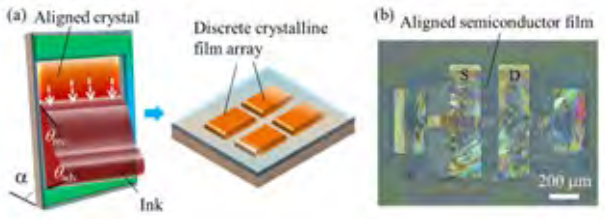

Fig. 1. Unidirectional dewetting of organic semiconductor ink by gravity-assisted dewetting. (a) Schematic illustration of aligned organic film formation by gravity-assisted dewetting. (b) Deposited aligned film of TIPS-Pentacene on printed Source/drain electrodes.

(2) Printable memory devices with DNA as a gate dielectric.

Printing device arrays of the non-volatile memory transistor is highly desired in the roll-to-roll manufacturing of integrated circuits. Here, we demonstrate the utilization of an insulating biomacromolecule of DNA in the printed transistor memory.[5] An insulating DNA derivative of DNA-OTMA was synthesized via a modified ion-exchange reaction in the aqueous solution. Homogeneous molecular orientation in DNA derivative was achieved through a solution process in butanol, which thus can be employed as the dielectric with a densely packed structure and a good insulating property. This allows us to fabricate integrated organic thin-film transistor (OTFTs) memories on a large-area flexible substrate at ambient atmosphere. Combining with the result of the low frequency dependence of capacitance and the long-time retention characteristic of more than 100 seconds, this solution-processed DNA-complex was revealed to be a ferroelectric-like dielectric. Besides, the printed memories exhibit hole mobility as high as 0.65 $cm^2V^{-1}s^{-1}$ and a large memory window up to 13 V. Therefore, this approach is promising for printing large-scale flexible OTFT memories and thus realizing highly integrated electronics (Fig. 2).

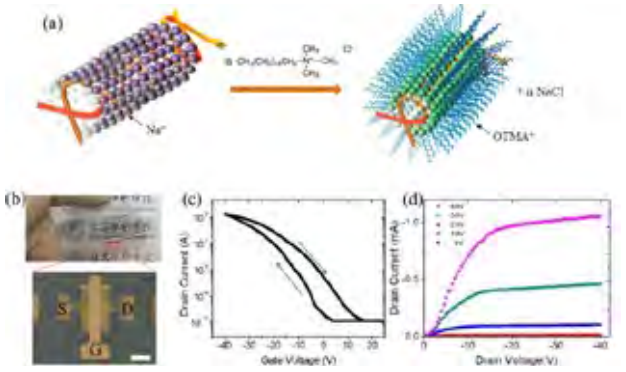

Fig. 2. Fully-printed OTFT memory devices with DNA-OTMA gate dielectric. (a) Schematic illustration of the preparation route for DNA-OTMA complex. (b) Fully-printed OTFT memory devices on a plastic substrate. (c), (d) Typical transfer and output characteristics of DNA-OTMA memory devices.

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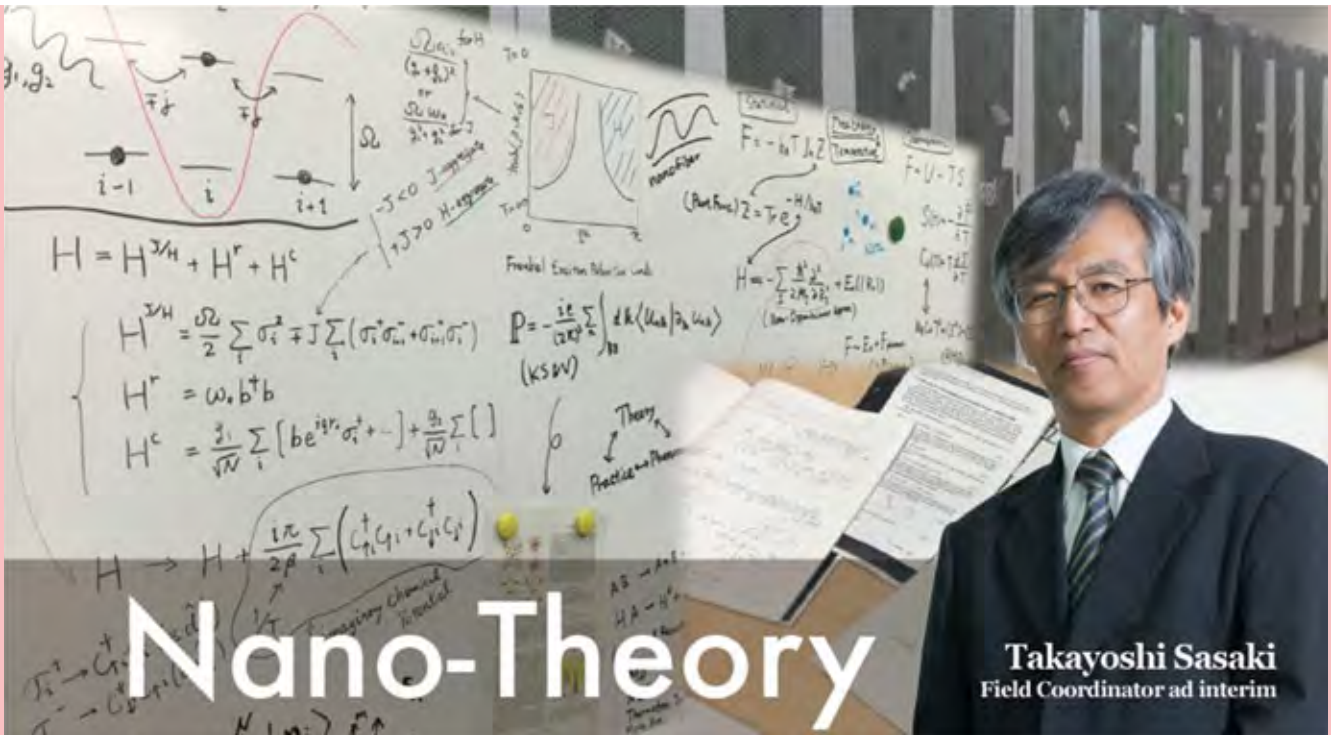

Understanding phenomena in the nanospace region, predicting new phenomena and creating novel nanostructured materials

Nano-Theory Field
(2 Research Groups)
- Materials Properties Theory Group
- First-Principles Simulation Group

Nanospace is a world in which common sense does not apply, where extremely small atoms are in motion, and electrons fly about in an even smaller space. Moreover, when huge numbers of these atoms and electrons act in coordination, they come to display behavior markedly different from those of single electrons and atoms. Ways of thinking and methods that are not bound by everyday common sense–namely, quantum mechanics and statistical mechanics–are essential for a proper understanding of the phenomena that occur there, and further, for devising new materials. Key activities in the field of nano-theory, which help achieve an understanding of the myriad phenomena emerging in nanospace, include building fundamental theories behind these novel behaviors by incorporating quantum mechanics and statistical mechanics, using our supercomputing facilities to obtain quantitative numerical predictions and develop new and efficient calculation methods. Besides providing interpretations of results obtained in other nanofield areas, we aim at invoking the outcomes of our research to predict as yet unearthed phenomena and to propose new materials featuring novel properties.


Theoretical Research Building

Material Properties Theory Group

Nano-Theory Field

Theory behind Nano-Originated Phenomena

Principal Investigator **Takayoshi SASAKI**
(MANA Director, Field Coordinator, Group Leader ad interim)
Takahisa Ohno (Senior Scientist with Special Missions), **Masao Arai** (Chief Researcher),
Wataru Hayami (Principal Researcher), **Kazuaki Kobayashi** (Principal Researcher),
Masanori Kohno (Principal Researcher), **Masamichi Nishino** (Principal Researcher),
Yoshihiko Nonomura (Principal Researcher), **Igor Solovyev** (Principal Researcher),
Shigeru Suehara (Principal Researcher), **Akihiro Tanaka** (Principal Researcher),
Junichi Inoue (Senior Researcher), **Junya Shimizu** (Principal Engineer)

1. Outline of Research

Ultimate aim of our research is to understand exotic properties and predict nano-structured materials with novel properties by utilizing theories and computational techniques based on the knowledge of nano-originated phenomena. Most of properties of material are in electronic states and/or collaboration among 10^{23} electrons. Thus, we study these issues by applying the quantum mechanics and the statistic mechanics with theoretical studies including topological analysis and the numerical computations, such as the density-functional theory (DFT) and Monte Carlo simulations.

2. Research Activities

(1) Nanomaterials.

By first-principles calculations, structural and electronic properties of various (nano-)materials were investigated.

- The ternary borocarbide $Sc_2B_{1.1}C_{3.2}$ has a layered structure with graphite-like BC_2 layers and NaCl-like Sc_2C layers stacked alternately. We revealed that B and C atoms are arranged to form $\sqrt{3}\times\sqrt{3}-R30°$ superlattices in the graphite-like layer.[1)]
- The nanostructured TiN(001)/MgO(001) superlattices (from 1x1 to 5x5) was predicted to exhibit various electronic properties depending on shape and size of the TiN dot and the MgO substrate.
- We started to accumulate theoretical vibrational spectra of typical geomaterials to assist structure identification of natural clay minerals closely related to agriculture, petroleum, catalysis, and waste shielding, etc.

(2) Topological Materials.

New class of materials with non-trivial topological numbers has been attracted wide attention. Various possibilities of realizations were investigated. From first-principles calculations, several hypothetical two-dimensional compounds, variants of MXenes, were predicted to be topological insulators. Utilizing the mathematical correspondence between small-capacitance superconducting islands and quantum spins, we found that a linear array of such superconductors, when appropriately biased by gate voltages, forms an artificial 1d topological insulator. In addition, we introduced an energy bunch Chern number defined for a bunch of connected bands. Its validity was demonstrated to three well-established previous results: (a)theorem of Chern number change, (b) bulk-edge correspondence and (c) a winding number of a point degeneracy.

(3) Strongly-correlated system.

Various anomalous electronic states observed in electron-doped and hole-doped high-temperature cuprate superconductors were collectively explained in terms of characteristics near the Mott transition through numerical investigation on the spectral properties of the two-dimensional *t-J* model with next-nearest neighbor hopping, which is an effective model of cuprate superconductors.

(4) Magnetism and related phenomena.

The microscopic theory, describing the behavior of electric polarization in non-collinear magnetic substances was developed and successfully applied for the analysis of magneto-electric effect, induced by the magnetic field in antiferromagnetic Cr_2O_3 and $BiFeO_3$, and properties of spin-spiral multiferroics $MnWO_4$, MnO_2, $CuFeO_2$, and MnI_2.[2)] In all these systems, the non-collinear magnetic order breaks the inversion symmetry and induces the electric polarization via the spin-orbit coupling.

We studied the phase diagram of an elastic interaction model for spin crossover materials with antiferromagnetic-like short-range interactions. We found that unusual"horn structures,"which are surrounded by ferromagnetic-like spinodal lines, disorder spinodal lines, and a critical line, are realized for relatively strong elastic interactions. We clarified that the interplay between the competing short-range and long-range (LR) interactions of elastic origin causes the unusual structures.

We generalized the cluster nonequilibrium relaxation (NER) scheme to quantum phase transitions simulated with the loop-cluster algorithm. As an example, the Neel-dimer quantum phase transition in the S=1/2 dimerized Heisenberg model on a square lattice was analyzed. The scaling form of physical quantities in the cluster NER scheme was derived theoretically, and applied to numerical analyses.

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First-Principles Simulation Group — Nano-Theory Field

Development of Large-Scale First-Principles Method and its Applications for Nano-Structured Materials

Principal Investigator **Tsuyoshi MIYAZAKI**
(Group Leader)
Ayako Nakata (Senior Researcher), **Jun Nara** (Senior Researcher),
Ryo Tamura (Researcher)

1. Outline of Research

We develop new theoretical methods to calculate physical properties and functions of complex nano-structured materials. Using the developed methods, we clarify the dynamical processes in the formation of nano structures, exotic properties of nano-scale materials, in collaboration with the experimental groups in MANA. We mainly use first-principles techniques based on the density functional theory (DFT). Machine-learning techniques are also used to predict the physical quantities of materials, and to realize efficient and reliable atomistic simulations.

2. Research Activities

(1) Development and applications of a linear-scaling first-principles molecular dynamics.

Conventional DFT methods cannot treat large systems comprising many thousands of atoms, since the calculation cost increases very quickly, proportional to the cube of the number of atoms N in the system. To overcome this size limitation, we have been developing a linear-scaling, or O(N), DFT code CONQUEST, jointly with the group of Prof. David Bowler. The code is extremely efficient on massively parallel computers, and we can treat very large systems containing more than 100,000+ atoms using the code. We recently established an efficient and robust molecular dynamics method with the linear-scaling technique used in the code. We have also implemented the constant temperature molecular dynamics method into the code[1] and applied this method to study the atomic structures of Si/Ge interfaces, including those in Si/Ge or Ge/Si core-shell nanowires. The study of core-shell nanowires is done in collaboration with Nanostructured Semiconducting Materials Group in MANA.

(2) Electronic structure analysis of large systems.

To analyze the electronic structures of large-scale systems efficiently, we combine the Sakurai-Sugiura method with CONQUEST.[2] In the method, the eigenstates in some specified eigenvalue region are calculated efficiently. This is suitable for practical applications because we need the information of the electronic structures only in some energy region of interest in most cases. Fig. 1 shows the calculated electron density distribution of the Ge hut cluster on the Si(001) surface, consisting of 23,737 atoms, around the Fermi level (Fig. 1). We can see that the electronic charge around the Fermi level is localized at the surface of the Ge hut cluster. The result is promising as an example of the electronic structure of one of the largest systems treated by first-principle DFT calculations.

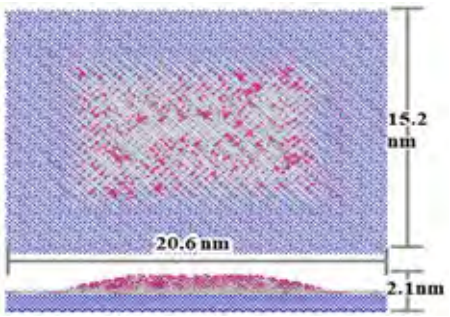

Fig. 1. Top and side views of the electronic density distributions of the Ge/Si(001) (23,737 atoms) with the energy window [-0.01:+0.02] eV around the Fermi level.

(3) Specific Information Extraction from the Smells.

By collaborating with Nanomechanical Sensors Group in MANA, we showed that the nanomechanical sensing combined with machine learning realizes the specific information extraction from the smells. Here, a newly developed nanomechanical sensor platform, a Membrane-type Surface stress Sensor (MSS), was utilized (Fig. 2). As a demonstration, we succeeded the alcohol content quantification from the smells of liquors by fusion of MSS, functional nanoparticles, and kernel ridge regression.[3]

Fig. 2: Extraction of specific information by combining nanomechanical sensor (MSS) and machine learning technique.

(4) Other developments and applications.

We also performed DFT studies to clarify the atomic and electronic structures of semiconductor surfaces,[4] metallic clsuters, organics solids at high pressures,[5] and so on.

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Nano-System Computational Science

Principal Investigator **Yoshitaka TATEYAMA**

1. Outline of Research

We are working on (1) developments of theoretical, computational and data-driven techniques as well as (2) understanding and design of materials and reactions crucial in the energy and environmental systems such as battery, catalyst and solar cell.

For the former issue, we're exploring the techniques for redox reactions, electron & proton transfer, and photo excitations with high-performance computing. In addition to density functional calculations, we're interested in data-science techniques as well as methods for larger scale phenomena.

Regarding the application calculations, our goal is to provide novel understanding of the microscopic mechanisms of the batteries, catalysts and cells, and suggest promising candidates for the next-generation technology. In particular, we focus on electrolytes as well as electrolyte-electrode interfaces, which play crucial roles in the energy storage and conversion.

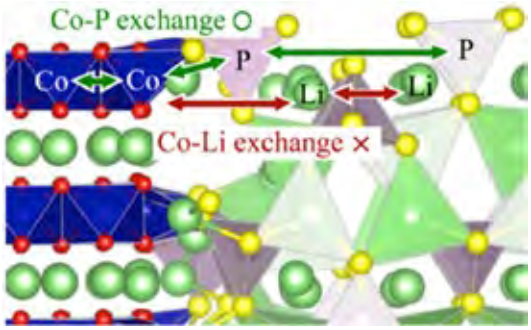

Fig. 1. A schematic picture of cation exchange at oxide cathode ($LiCoO_2$) and Li_3PS_4 sulfide electrolyte. The Co-P exchange is found to be thermodynamically stable.

2. Research Activities

In this year, we proceeded the understanding of solid-solid interfaces in all-solid-state battery and perovskite solar cell.[1,2] As solid-solid interface structures can't be property examined by molecular dynamics, which plays a crucial role for liquid-solid interfaces, we developed another simple procedure to explore a variety of interface matching. Then, we found that the depletion growth of Li ions still holds even if the cation exchanges occur (Fig. 1). For the solar cell, we elucidated the band alignment and carrier transfer at the interfaces (Fig. 2). We also joined the development of bulk structure search via the AFIR technique as well.[3]

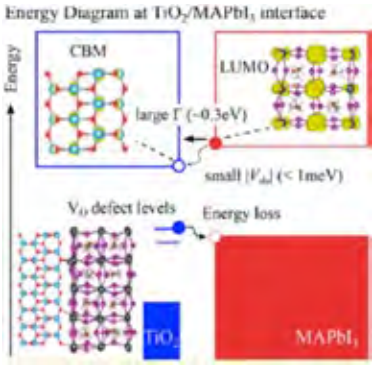

Fig. 2. A schematic picture of TiO_2 electrode / $CH_3NH_3PbI_3$ perovskite materials interfaces and the band alignment.

For the collaborations with experimentalists, we have made several crucial contributions. For the battery electrolyte, we found "extinguisher" type novel superconcentrated electrolyte for Li and Na ion batteries (Fig. 3).[4,5] We also elucidated the reduction – oxidation mechanisms of Boron-doped diamond electrode.[6]

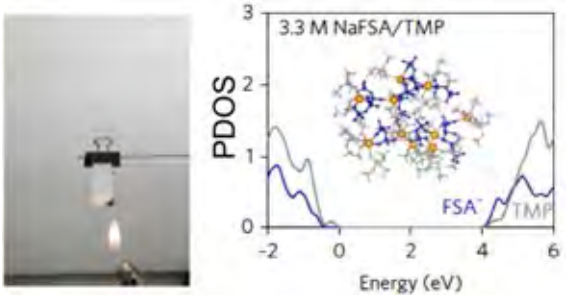

Fig. 3. (left) Safety (burning) test of the newly developed electrolyte. (right) Projected DOS of 3.3M NaFSA/TMP electrolyte, indicating the sacrificial anion reduction.

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MANA Satellite | Nano-Theory Field

Development of O(N) DFT, and Study of Semiconducting Nanowires on Surfaces

Principal Investigator **David BOWLER**
(MANA Satellite at UCL, UK)

1. Outline of Research

Our ultimate aim is to understand advanced nano-structured materials for applications in photovoltaic devices, as well as future electronic devices. . Our research combines close collaboration with experiment and theoretical modeling to give a detailed insight into the properties of the materials. In our first satellite project, we investigated how to combine biological inspiration with electronics to give high efficiency materials and solar cells with applications to energy and sustainability. In our present project, we are studying the growth and properties of silicon-germanium nanostructures, both nanowires and clusters formed on surfaces, to optimize their characteristics, particularly concentrating on the mobility and location of dopants. We are also continuing to study biological systems, to seek inspiration for hybrid solid-state/biological nano-architectures.

We are leading the development of *ab initio* methods that can be applied to large systems. Much of our research involves development of the CONQUEST linear scaling DFT code, which has been developed through a long-term collaboration between UCL and NIMS, and is now expanding to include other sites around the world.

We have a long-established network of collaboration between MANA in NIMS, and the London Centre for Nanotechnology in University College London. In this year, we have arranged collaborative research visits to MANA for the PI and the MANA UCL student, as well as visits to UCL from researchers in NIMS.

We are also expanding our international links, collaborating with the Institute for Molecular Science in University of Bordeaux and Osaka University, in a four-way exchange of personnel and expertise.

2. Research Activities

(1) Properties of Bi nanolines on Si(001).

We have continued our research on the exceptionally straight Bi nanolines that form spontaneously on Si(001), working with both experiment (in Geneva) and theory (in NIMS as well as UCL) to characterize the electronic structure of the nanowires and their interaction with the surrounding silicon.[1)] We have also characterized a feature found on these lines which appears to show sub-atomic detail[2)] (Fig. 1). This feature is formed dynamically by the back-and-forth flip-flop of a silicon dimer substituted for a Bi dimer.

We have also explored how these lines might be used to perform delta-doping of Bi into silicon,[3)] and found that the capping and post-growth treatment of the sample is key to the activation of the Bi dopants, which can be included at densities of up to 1/8 ML.

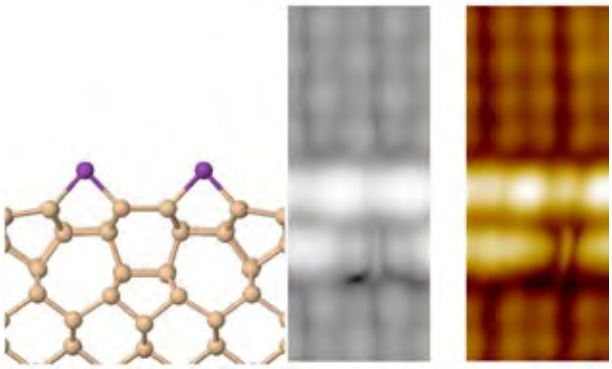

Fig. 1. Left: The Bi nanoline structure in profile. Right: Comparison of modelling (grey) and experiment (orange/brown) for sub-atomic feature on Bi nanolines.[2)]

(2) Development of novel methods.

As well as the important area of applications and collaboration with experiment, our research is based around extending and improving the CONQUEST code. We have recently collaborated with a group in Tsukuba University to implement and approach to finding eigenstates and energies even from large, O(N) calculations where this is not normally possible, as shown in Fig. 2. We also continue to improve the molecular dynamics implementation, showing thermostats with linear scaling DFT.[5)]

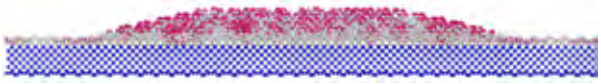

Fig. 2. Side view of a germanium nanocluster on silicon (Ge in grey, Si in blue) showing the charge density (pink) for the states near the Fermi level.[4)] The model contains 23,737 atoms.

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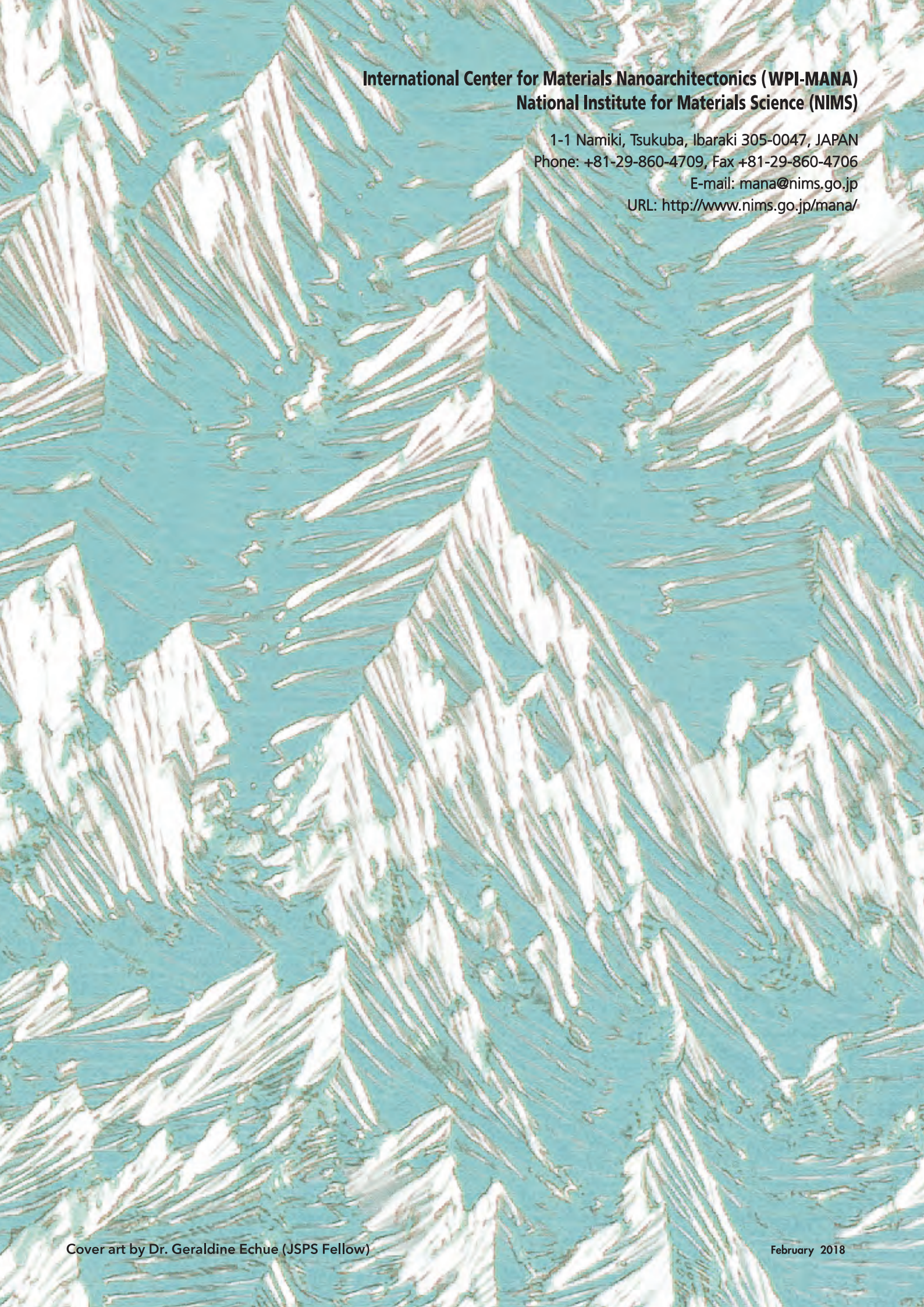

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