from Tsukuba, Japan to the world

NIMS NOW International

National Institute for Materials Science

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RESEARCH FRONTIER

Fabrication of Nano-Dendritic Structure with Branches under 3 nm

—Fabrication of novel nanostructure using electron beam—

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Research to impart unique properties to materials and discover new functions by controlling the surface structure and composition at the nano-level is increasingly required. Furthermore, because there is also a possibility that the fabricated structures themselves can be applied practically as devices, processes for fabricating various nanosized structures by controlling size at arbitrary positions are being widely researched. Although fabrication technologies for nanowires, nanodots, and other nanostructures have been reported, to date, there has been no method of fabricating dendritic structures in the nanosize region.

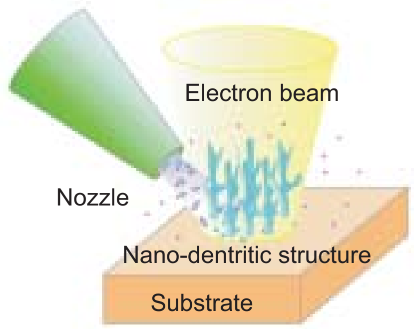

Fig. 1: Schematic diagram of fabrication apparatus for nano-dendritic structure. Metal gas (blue, red) from the nozzle is decomposed by the electron beam, and the metal atoms (blue) grow in a dendritic structure.

We succeeded for the first time in the world in fabricating a nanosized dendritic structure with branches under 3 nm by decomposing organometallic gases under electron beam (EB) irradiation and using the vapor deposition properties of that these metals and their compounds. Concretely, using a 200 kV transmission electron microscope, we performed EB irradiation in the nanosize region of an insulator substrate with a micro-diameter electron beam and control of the irradiation position with nanometer precision. We also fabricated nano-dendritic structures on the substrate by delivering a gas containing the target element to the vicinity of the substrate with a newly-developed gas delivery system while maintaining a high vacuum in the electron microscope sample chamber. **Fig. 1** shows a schematic illustration of the fabrication apparatus.

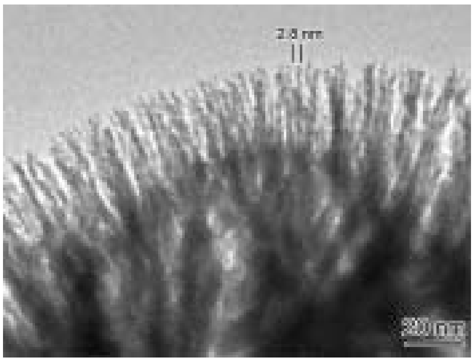

Fig. 2: Tungsten (W) nano-dendritic structure grown under electron EB.

Fig. 2 shows an example of the results of the actual process. $W(CO)_6$, which is a type of organometallic gas, was introduced around the surface of a substrate of Al_2O_3, which is a type of insulator. When the substrate was irradiated with the electron beam, a nano-dendritric structure grew. (**Fig. 3**) The wire-shaped substances which can be observed in the figure are the branches of the nano-dendritic structure. The diameter of the smaller branches is less than 3 nm. < Continued on p.2

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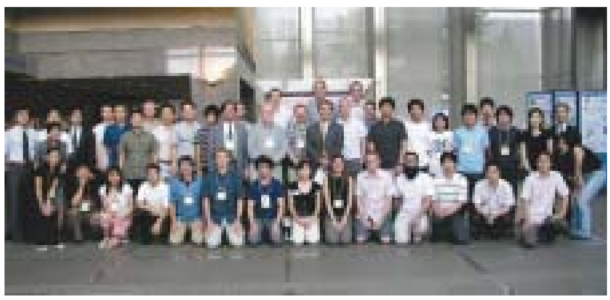

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New Analytical Method for Local Structure/ Surface State using Photoluminescence

Hiromitsu Nakajima, Toshiyuki Mori
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Ecomaterials Center (EMC)

Because photoluminescence (PL) reflects the structure and state of the substance generating PL and the environment in which that substance is placed, it is possible to analyze the structure of substances and state of their surfaces by investigating PL.

Yttria-stabilized zirconia (YSZ) is an extremely important material for industry, as it is used in sold fuel cells and other applications, but because it is difficult to investigate the relationship between its properties and local structure, points requiring study remained. We therefore attempted an analysis of its local structure using trace impurities (on the order of less than 1 ppm) which are unavoidably included in YSZ as a PL probe. In measurements of the PL of YSZ, terbium (Tb), which is one of these trace impurities, showed two PL excitation peaks, and it was found for the first time that a linear relationship exists between the wavelength difference of these two peaks and the concentration of Tb in the YSZ (**Fig. 1**). Based on this result, it is possible to estimate the amount and distribution of local lattice defects in the vicinity of Tb, the Coulomb potential, etc. without destructive testing or pretreatment. Moreover, it is expected to be possible to clarify the relationship between the local structure and Coulomb properties by comparing information on these local structure and their Coulomb properties. It also appears that the same type of analysis can be performed using other light-emitting impurities in YSZ.

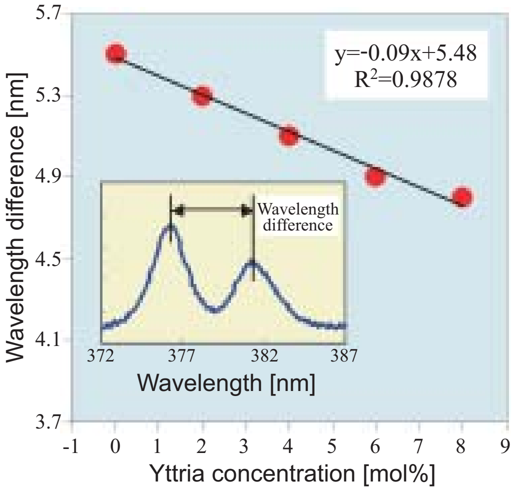

Fig. 1: Relationship between difference in wavelengths of two PL excitation peaks of Tb and yttria concentration. (The insert shows an example of the two peaks of Tb.)

On the other hand, while titanium dioxide (TiO_2) has drawn considerable attention as a photocatalyst in recent years, an adequate understanding of the relationship between the state of the TiO_2 surface and adsorption has still not been obtained. It is considered possible to produce photocatalysts with higher activity if this relationship is clarified. Therefore, we investigated the relationship between PL and adsorption in TiO_2. In experiments using ethanol (EtOH) as the adsorbate, it was found that a linear relationship exists between the reciprocal of the PL intensity of TiO_2 and the reciprocal of the EtOH concentration (**Fig. 2**). These results mean that adsorption of EtOH on the surface of TiO_2 can be described by a simple Langmuir isotherm, and PL intensity increases in proportion to the percentage of the TiO_2 surface covered by EtOH, thus showing for the first time that phenomena related to adsorption on TiO_2 surfaces can be investigated quantitatively using PL.

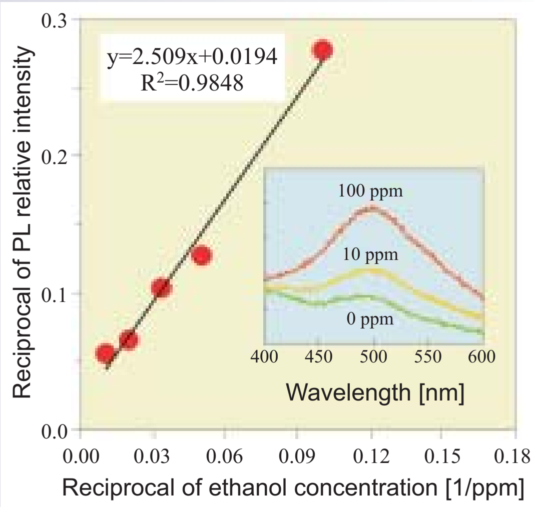

Fig. 2: Relationship between PL intensity and ethanol concentration of aqueous suspensions of TiO_2 particles. (The insert shows examples of the PL spectra of the suspensions.)

In the future, we plan to investigate the local structures and surface states of various substances using the new PL analysis method described above and utilize the knowledge gained to design high-function materials.

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Fabrication of Nano-Dendritic Structure with Branches under 3 nm

Among the properties of this nano-dendritic structure, it consists mainly of the target elment, contains a large number of nanosized crystal particles, displays electrical conductivity, has many nanosized branches, and has an extremely large specific surface area. Furthermore, the size of the structure as a whole and the location of formation can be controlled easily, and combinations of numerous types of substrates and gas sources are possible. Considering these features, these research results are expected to find wide application in research and development of surface-effect devices, sensors, nanosized catalysts, and fabrication and arrangement of structures for catalyst carriers, and in fields such as chemistry, biology, pharmaceutical manufacture, and others.

For further information, please visit: http://www.nims.go.jp/hvems/

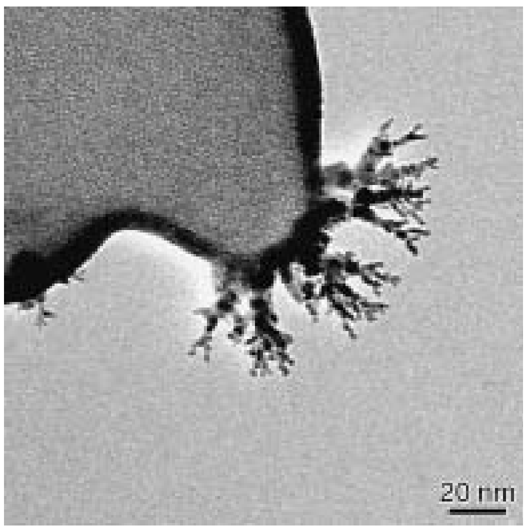

Fig. 3: W nano-dendritic structure fabricated on an Al_2O_3 substrate by EB-induced vapor deposition.

Statistical Treatment of Corrosion Modes using CCD Laser Displacement Sensor

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Corrosion Group
Materials Information Technology Station (MITS)

The laws of the natural world dictate that metals such as iron and steel materials unavoidably form oxides and other corrosion products as a result of corrosion reactions. Corrosion modes can be broadly divided into general corrosion and local corrosion. General corrosion, as the name suggests, is a type of corrosion in which the entire surface is consumed by corrosion uniformly, and is frequently seen in carbon steels in the atmosphere outdoors. On the other hand, corrosion which proceeds locally is called local corrosion; a representative example is pitting corrosion on stainless steel. In order to treat the above-mentioned corrosion modes (surface roughness) as numerical data, we attempted to develop an index of the corrosion mode depending on the corrosion environment by digitalizing corrosion phenomena using a surface profile measuring device and performing extreme-value statistical treatment.

The surface profile measuring device (**Fig. 1**) which we used combines a CCD laser displacement sensor with high-precision X, Y, and Z axis stages. **Fig. 2** is an example of measurement using this device, and shows the surface of electrolytic iron when the rust was removed after a 2-year exposure test at Miyakojima. The central part (40 x 40 mm) of the test piece surface (150 x 50 mm) was measured at intervals of 100 µm and expressed 3-dimensionally based on data for 401 x 401 points (total: 160,801 points).

The data measured as shown in **Fig. 2** were divided into 256 equal meshes, and the maximum corrosion depth in each mesh was obtained and arranged by extreme-value statistical processing (assumed to conform to a Gumbel distribution). The results are shown in **Fig. 3**. It can be understood that a single linear relationship is materialized with electrolytic steel, which shows all-over type corrosion, whereas linear relationships lying along 2 lines are obtained with Fe-3% Cr alloy. The line (red) showing a large corrosion depth represents pitting, while the second line (blue) represents general corrosion. Thus, these results show that two types of corrosion proceed simultaneously in the case of the 3% Cr alloy.

Because the corrosion profile closely resembles topographical data, an explanation in terms of fractal theory may be possible. Future study of this point is planned.

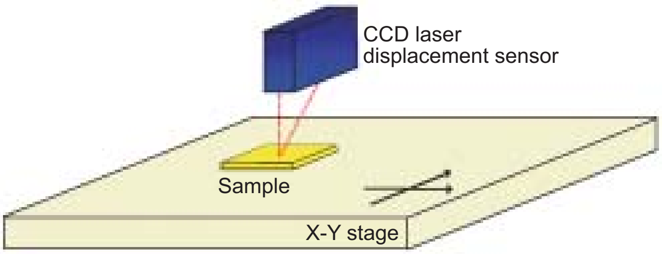


Fig. 1: Schematic illustration of surface profile measurement device.

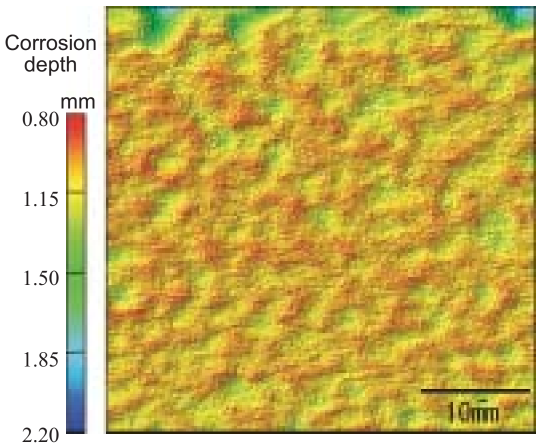


Fig. 2: Example of measurement of surface profile: electrolytic iron exposed for 2 years at Miyakojima.

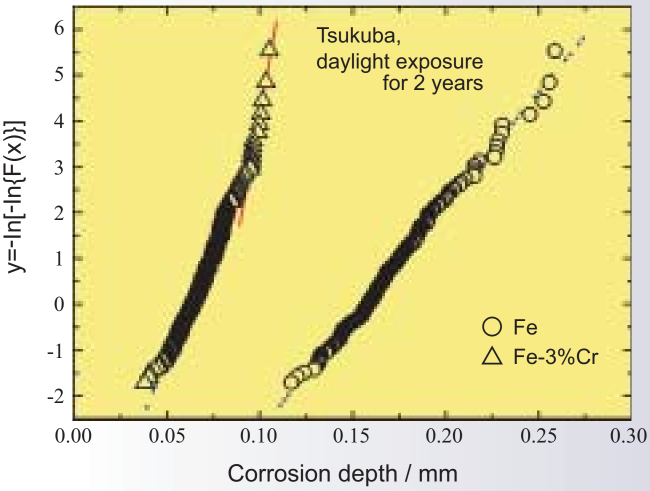


Fig. 3: Example of surface profile data arranged by Gumbel plots.

For further information, please visit: http://www.nims.go.jp/corrosion/index_e.html

Visit by South African Ambassador

On August 18, the South African Ambassador to Japan, Dr. Ngubane, visited NIMS. As announced in the last issue, NIMS and South Africa agreed to cooperate in research on superalloys and signed MOUs in May of this year, and have also begun studying nanotech-related cooperation. The ambassador had a talk with President Kishi of NIMS and, after a briefing on the Biomaterials Center (BMC), inspected a research laboratory for high temperature materials.

Synthesis of Cesium Titanate Single Crystal by Fused-Salt Electrolysis

—Treatment of radioactive waste by electrochemical method—

Hideki Abe
Materials Physics Group
Materials Engineering Laboratory (MEL)

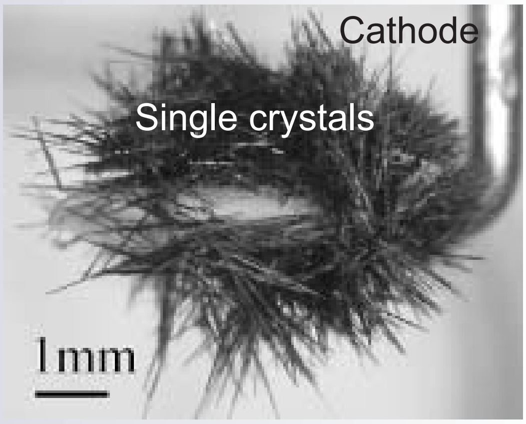


Fig: Single crystals of $Cs_xTi_8O_{16}$ synthesized by fused-salt electrolysis.

Cesium 137 (^{137}Cs), which is contained in high level radioactive waste, is not only highly toxic to living organisms, but is also easily vaporized and has high solubility in water due to its easy ionization. As a result, it causes widespread environmental pollution by circulation in the atmosphere and hydrosphere. To prevent diffusion into the environment, it is essential to immobilize ^{137}Cs in a stable solid compound and inter it after solidification.

Cesium titanate hollandite $Cs_xTi_8O_{16}$ (x = 1.0-1.35) is known as a compound which enables stable immobilization of Cs ions. Therefore, the development of a synthesis process for $Cs_xTi_8O_{16}$ with the highest possible concentration of Cs ions has been an important problem for research in nuclear fuel chemistry.

Synthesis of $Cs_xTi_8O_{16}$ is normally performed based on a direct reaction between titanium oxide, TiO_2, and either elemental Cs or Cs oxides under a high temperature of 1250 ℃ to 1500 ℃. In this process, it is necessary to enclose the materials in a heat-resistant, airtight metal container in order to suppress transpiration of Cs accompanying this high temperature reaction. However, because it is generally difficult to realize large scales with closed high temperature processes, the conventional synthesis process was not suitable for actual waste treatment sites, which handle large quantities of radioactive wastes.

We recently developed a process for synthesizing single-crystal $Cs_xTi_8O_{16}$ with a high Cs concentration below 1000 ℃ in a system that is open to the air using fused-salt electrolysis.

First, a mixed fused salt is produced by dissolving TiO_2 at a mol ratio of 1:10 in cesium molybdate (Cs_2MoO_4) melted at 950 ℃. Electrolysis is then performed for 1 hr by applying a voltage of several volts. As a result, needle-like single crystals of $Cs_xTi_8O_{16}$ are synthesized on the cathode (see **figure**). The results of analysis showed that a high concentration of Cs ions, achieving the upper limit on the Cs ion content in $Cs_xTi_8O_{16}$, x = 1.35, was immobilized in the single crystals.

Because the Cs ion immobilization process using fused-salt electrolysis has the advantages of moderate reaction conditions and a simple synthesis device, it is considered applicable to radioactive waste treatment at the industrial level.

Events Commemorating Completion of the Nano-Biomaterials Research Building

On July 16, NIMS held a series of events commemorating the completion of the Nano-Biomaterials Research Building at the Namiki Site, including Memorial Lectures, a tour of the facilities, and a reception, which were attended by 193 persons.

Speakers presenting Special Memorial Lecture series were Dr. Koichi Kitazawa, Executive Director of the Japan Science and Technology Agency (JST), Dr. Masakazu Aono, Director-General of the Nanomaterials Laboratory (NML), and Dr. Junzo Tanaka, Director-General of the Biomaterials Center (BMC). During the facility tour, many participants visited the new Nano-Biomaterials Research Building, which was opened to guests as an open laboratory, and at the reception, persons involved in the construction were recognized. Although held on a rainy day, this was a fitting completion celebration for the new building.

Reconsideration of GaAs Surface Structure

—From proposal of a new structural model toward surface structure control—

Akihiro Ohtake
Nanodevice Group
Nanomaterials Laboratory (NML)

When the structure of a bulk material is exposed, the interatomic bonds at the surface of solid crystals are broken, and as a result, the appearance of a different structure is not uncommon. This tendency is remarkable in substances with strong covalent bonds, and in some cases, the 2-dimensional unit cells of the surface differ from the bulk. This type of surface is called a reconstructed surface.

The cleaned (001) plane of gallium arsenide (GaAs), which is a representative compound semiconductor, also manifests a reconstructed surface, and various structures may appear, depending on the composition ratio of gallium (Ga) and arsenic (As) at the surface. It has long been known that a structure called c(4x4) appears on surfaces with the highest As concentration. Because this surface is also used in fabricating quantum dots on a GaAs (001) substrate, there is considerable interest in its atomic arrangement. As a result of long years of research, as shown in **Fig. 1(b)**, a structure consisting of three As dimers per surface cell structure (As-As dimer structure) was proposed. Because this structure is mentioned in a number of textbooks, virtually no one had questioned its appropriateness.

Nevertheless, after a detailed investigation of this surface, we found many contradictions in the experimental results regarding this As-As dimer structure, not only in our own work, but also in past experimental results. Normally, a c(4x4) surface is fabricated by reducing the substrate temperature under As_4 molecule beam irradiation. However, in scanning tunneling microscope (STM) observation of c(4x4) surfaces fabricated by this method (**Fig. 2(a)**), we discovered that Ga-As dimers, and not As-As dimers, exist on this surface (**Fig. 1(a)**). The appropriateness of the Ga-As dimer structure model was also confirmed by various experimental methods, beginning with electron refraction, and by first-principles calculations.

We also succeeded for the first time in controlling the surface structure by changing the type of As molecule used when fabricating the c(4x4) surface. When As_4 molecules are dissociated to form As_2 molecules and these were used to fabricate the (c4x4) surface, it was found that the As-As dimer structure, which had been proposed previously, does in fact appear (**Fig. 2(b)**).

These results not only provide fundamental knowledge for elucidating the mechanism of surface reconstruction, but are also expected to offer important basic information for fine control of nano-structure formation on GaAs surfaces.

(Results related to this research have been published twice in *Phys. Rev. Lett.* and once in *Appl. Phys. Lett.*)

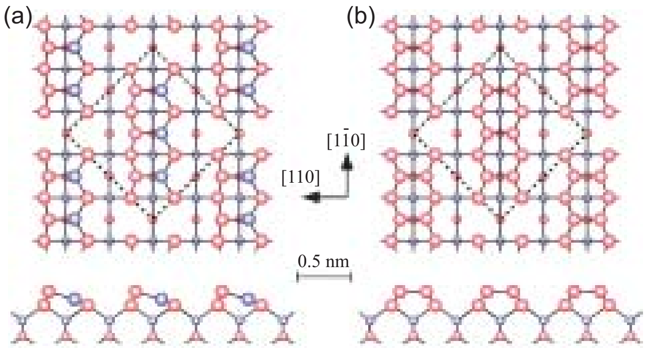


Fig. 1: Surface reconstruction models for GaAs (001)-c(4x4)
(a) Ga-As dimer structure, (b) As-As dimer structure.

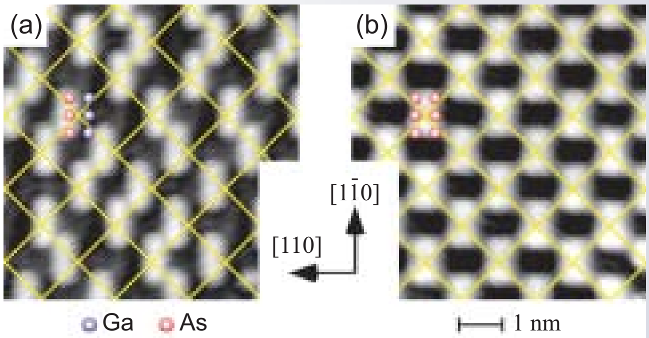
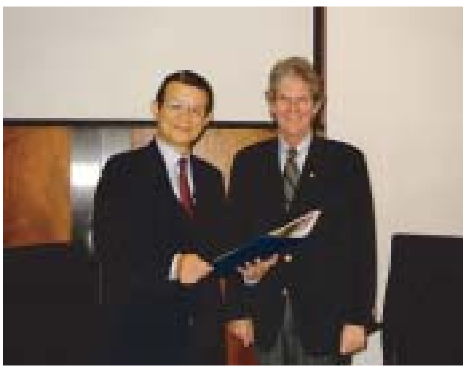


Fig 2: STM images of the GaAs (001)-c(4x4) surface (filled-state images)
(a) Ga-As dimer structure, (b) As-As dimer structure.

For further information, please visit: http://www.nims.go.jp/nanomat_lab/ResGroup/Device/device.html

NIMS to Expand Cooperation with Five Australian Universities

NIMS will strengthen its alliance with a group of five Australian universities (Sydney, Queensland, New South Wales, Melbourne, and Western Australia Universities). Although a Joint Graduate University agreement was concluded with the five universities in August of last year, under the new agreement, NIMS plans to promote joint international research by expanding to scope of cooperation to the teaching staff of the five Australian universities and NIMS scientists.



On July 9, President Kishi of NIMS and representatives of the five universities held a television conference at Queensland University to consider concrete measures for strengthening cooperation. As a result, the two sides agreed to strengthen publicity on exchange programs such as the Joint Graduate University system and the NIMS International Center for Young Scientists (ICYS), appoint "matchmakers" to promote cooperation from among NIMS researchers, and establish a NIMS office in Queensland University to promote cooperation, among other measures.

On the same day, Prof. John Hay, Vice-Chancellor and President of Queensland University, bestowed the title of Professor Emeritus on President Kishi.

NIMS Summer Events

< Continued from p.1

First Japan-UK Nanotechnology Summer School

The First NIMS-IRC Nanotechnology Summer School was held at NIMS July 26-30. The IRC, or Interdisciplinary Research Collaboration project, is sponsored by UK's Research Councils. For this event, 18 graduate students visited Japan from University of Cambridge, University College London, and University of Bristol, which are participating in the IRC in Nanotechnology, and presented the results of recent research in turn with 18 counterpart Japanese graduate students who are conducting research at NIMS. Sessions were characterised by lively discussion. While deepening their knowledge of leading-edge nanotechnology, the participating students also formed personal ties through a friendly football match, NIMS summer evening festival, and climb up Mt. Tsukuba. The Second Summer School is scheduled to be held next summer at Cambridge. NIMS also hopes to foster a new generation of leading materials researchers by creating opportunities for international exchanges of young scientists in the future.

Science Camp 2004

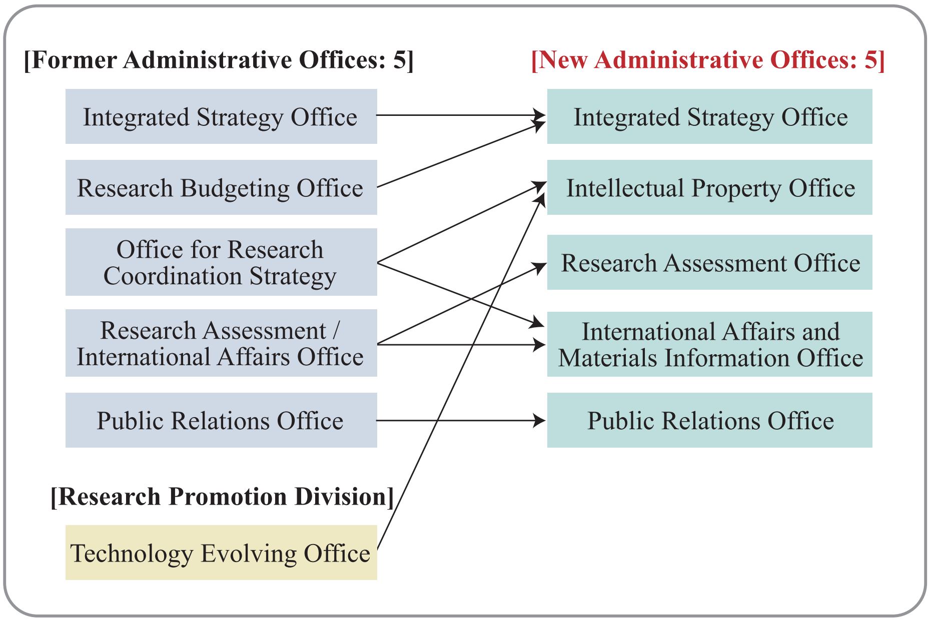
NIMS held its Science Camp 2004 from July 28-30. Fifteen high school students from all parts of Japan gathered at NIMS to study advanced research.

The 1st day of the Camp began with an Opening Ceremony at the NIMS Sengen Site, followed by experiments on metal fracture using the creep tester and various other experiments. On the 2nd day, activities moved to the Namiki Site. The rainy day featured enjoyable experiments in the creation of diamonds and polymers, making metals by pewter-craft, etc. On the 3rd day, the Camp returned to Sengen for the remaining experiments and presentations summarizing the research studied during the three days, and Summer Camp 2004 concluded successfully. NIMS hopes that this event will inspire a future generation of world-class research with an interest in materials research.

Mini-Doc Course for Middle School Students

NIMS held a mini-doctorate course for middle school students over a 3-day period from August 3 to 6 with 5 students from each of the middle schools in Ibaraki Prefecture. The students enjoyed experiments with NIMS researchers, who served as instructors, in a friendly atmosphere and participated in the program quite enthusiastically, as seen in questions about the experiments and future developments that went on well past the end of the sessions. On the final day, some students expressed their hope to participate in the course again next year. Thus, the curtain came down on the NIMS Middle-School Mini-Doc Course for 2004 with a general feeling of great accomplishment and promise.

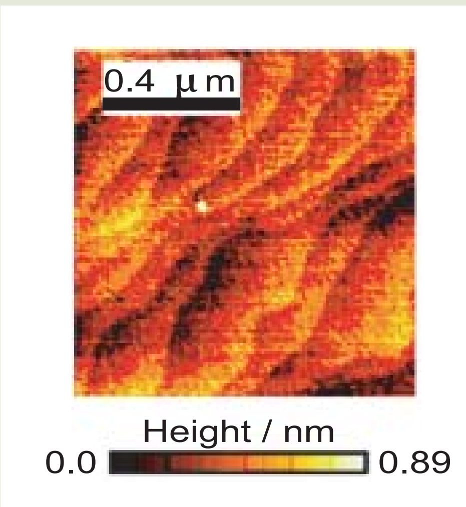
Reorganization of Five Administrative Offices at NIMS



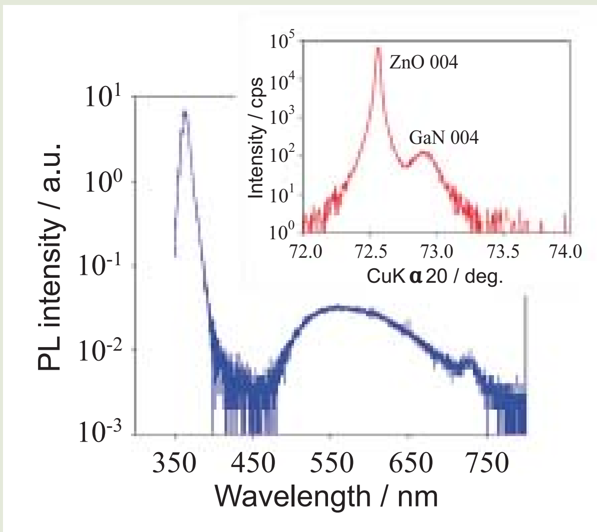
Effective August 1, NIMS carried out a partial reorganization of its planning-related section. As a central organization for materials research in Japan, NIMS is now working out new policies for promoting activities in this field. This reorganization was part of the same effort and has the following aims. First, the Integrated Strategy Office absorbed the Research Budgeting Office in order to unify acquisition of research funds and allocation/ coordination of research resources. A new Intellectual Property Office was created to handle business related to technology licensing and consulting. The purpose of this move is to utilize intellectual property created by NIMS strategically and tactically, and in particular, to cooperate more closely with private-sector companies. Next, the Research Assessment/ International Affairs Office was split into a Research Assessment Office and a separate International Affairs and Materials Information Office. The Research Assessment Office will be responsible for assessing institutes, R&D results, and individual achievements, while the International Affairs and Materials Information Office will endeavor to strength international cooperation and improve the materials-related information collection/analysis/ dissemination functions. The Public Relations Office was not affected by the changes.

Launch of New Venture Business NIMSWave

A new venture business called NIMSWave was launched on May 26 with participation by researchers involved in zinc oxide-related materials from NIMS, Tokyo Denpa Co., Ltd., and Tohoku University and has become a NIMS-authorized venture company. The company will develop and commercialize advanced application technologies for ZnO single crystal substrates, which are expected to make an important social contribution.



AFM image of the atomically flat ZnO substrate.



X-ray diffraction and photoluminescence of GaN/ZnO structure.

■ Doing Research in Japan ■

Yarong Wang (China)
Research Fellow (Jun. 2001-present)
Eco-Energy Materials Group, Ecomaterials Center (EMC)

I'm Yarong Wang from China. Glad to have this chance to introduce myself. I came to Japan in the autumn 7 years ago as a Doctor-course student supported by Monbusho scholarship. After getting doctor degree in solid-state chemistry from Tohoku University in the spring of 2001, I started to work in NIMS as a Research Fellow. I've lived in Tuskuba city for a little more than 3 years up to now, and I love this small, quiet, but open-minded city very much. In my personal opinion, it might be the best place to live in Japan.

Since joining NIMS, I have been working with Dr. Toshiyuki Mori in the eco-energy group doing research on the synthesis of ceria-based solid electrolytes via wet-chemical route as well as their characterization. The key point in my work is to get ultra-fine and well-dispersed powders so that densification of the solid electrolytes (usually >1500 ℃) can be achieved at significantly lowered temperatures (presently ~1100 ℃). This not only allows energy saving in the fabrication process, but also permits microstructure and hence electrical property tuning of the sintered bodies. I like the present research ideas. The wet-chemistry route might be complicated but it is flexible and full of possibility. Material design of solid electrolytes, on the other hand, is full of dreams.

■ A Detailed Manual for Kindergarten Sports Festivals ■

I'm Bong-Chull Kim, a Research Fellow at NIMS. I'm interested in the research fields of advanced Li-ion secondary batteries and nano-sized powder fabrication using high energy milling and laser ablation.

Bong-Chull Kim (South Korea)
Research Fellow (Apr. 2004-Mar. 2007)
Soft Chemistry Research Group
Advanced Materials Laboratory (AML)

[At the Sports Festival]

I am the father of a very pretty daughter (5 years old) and a wild son (3 years old). My family moved from Korea to Japan 3 years ago, when my son was only 4 months old. The trip was hard work for us, and was especially hard on my son, who was seriously ill for a week. My family started life in Japan by struggling with many problems like this. Now we are well adapted to our new circumstances in Japan and even feel more comfortable in Japan than in my country.

Last year, my wife signed me up as a volunteer for the sports festival at my daughter's kindergarten (without asking me!), and I helped the teachers at her school with the preparations. While I was working together with them, I saw their 50-page manual, which gave many tips for a successful event. For example, the place to pitch a tent, entrance and exit, and all the programs were described in detail. I also heard that the manual has been revised and improved every year after the festival. I regard it as the most flawless manual for a sports festival in the world! That's one of the experiences in which I felt Japanese sincerity and the traditional mind.

Yamaboshi
(Cornus Kousa)

Yamaboshi is a deciduous tree native to East Asia. There are some Yamaboshis in NIMS and they welcome visitors with beautiful white flowers in spring and with small orange fruits in autumn.

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