



# IMS NOW

## International

National Institute for Materials Science

Vol.4 No.12 December, 2006

### Special Features

Introduction of 20 New Projects and Recent Achievements - Quantum Beam Center (QBC) -

## Quantum Beam Basic Technologies for Creation/Characterization of Nanomaterials

To meet social demands for nanotechnology, energy, environment and other issues, research and

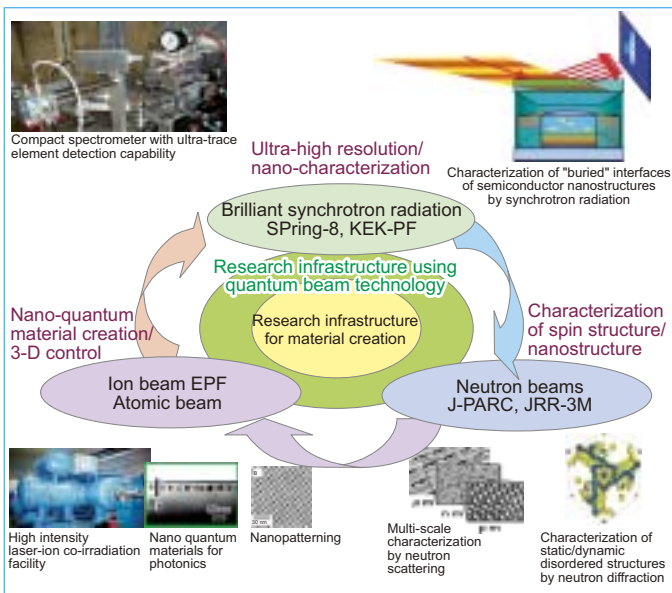


Fig. Development and use of quantum beam basic technologies for creation/characterization of nanomaterials.

Naoki Kishimoto  
Managing Director  
Quantum Beam Center (QBC)

development of nanomaterials with innovative functions is indispensable. Such functions include ultra-fast, ultra-high density quantum functions, nonlinear optical properties, magnetic/dielectric properties, photoelectric conversion and so on.

The Quantum Beam Center is engaged in comprehensive development/utilization of advanced beam technologies with the aim of realizing breakthroughs in

material creation, fabrication, control, and characterization. Our work focuses on quantum beams, which are particularly powerful techniques for achieving these goals, and includes brilliant synchrotron radiation, neutron beams, ion /atomic beams. As shown in the figure, our aim is to establish the basic technologies for materials science in the fields of quantum beam technology by utilizing the NIMS R&D potential for material creation/characterization.

< Continued on p.2

## NIMS News



### MOU with Universidad de Chile

(October 3, NIMS) -- NIMS' International Center for Young Scientists (ICYS) and Nanoscale Materials Center signed an MOU with the Center for Advanced Interdisciplinary Research in Materials (CIMAT), Universidad de Chile, Chile. This MOU is for collaboration on the exploratory research of new functional materials with CIMAT.



From the left: Prof. Sasaki, Managing Director of Nanoscale Center, Prof. Bando, Director General of ICYS, Dr. Lund, Director of CIMAT, and Dr. Murase, Senior Researcher of ICYS.

### in this issue

Quantum Beam Basic Technologies for Creation/Characterization of Nanomaterials	1
Atom Beam Lithography	2
Development of Nanomaterials Using Ion Beam Technology	3
Development of Nanomaterials Using Neutron Beam Technology	4
Realtime Observation of Surfaces and Buried Interfaces of Thin Films and Multilayer Films	5
Process for Simultaneous CO <sub>2</sub> Reduction and H <sub>2</sub> Production	6
Materials Science Research Using Synchrotron Radiation	6
Advanced Crystal Analysis Using Synchrotron Radiation	7
NIMS News	1, 4, 5
Hello from NIMS	8

# Atom Beam Lithography - Nanofabrication Using Metastable Atoms and Self-Assembled Monolayers -

Yasushi Yamauchi, Mitsunori Kurahashi  
Taku Suzuki  
Atomic Beam Group  
Quantum Beam Center (QBC)

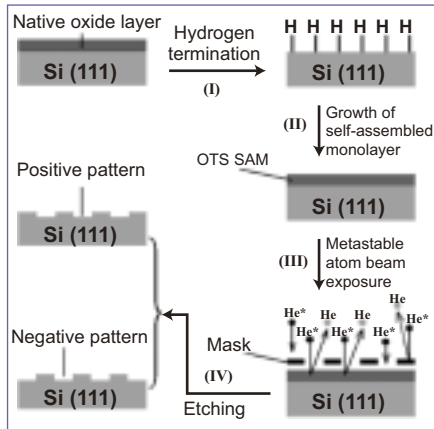


Fig. 1 Atom beam lithography process.

Microfabrication by lithography is a suitable technique for mass production of high-density integrated semiconductor devices. Since the birth of this technology, light had been used as the exposure source, and a polymer such as polymethyl-methacrylate (PMMA) had been used to form thick resist layers. Although various factors limit microfabrication in lithography, most of these have been solved, and microfabrication has been achieved to the diffraction limit of light. Because the diffraction limit depends on wavelength, short wavelength UV light is now used. Soft X-rays, electron beams, and other types of beams that have even shorter wavelengths are also being investigated and have been used in small-lot trial production.

However, to continue miniaturization in mass production into the future, fundamental solutions to various problems will be required, not limited to the diffraction limit of the exposure source, but also including overcoming penetration and proximity effects, introduction of thin film resists suited to the

fabrication width, etc. In contrast to this, atomic beams of a thermal velocity (100 meV) which has complementary properties with other quantum beams such as highly transmissive X-rays do not have penetration problems and are sensitive to the topmost surface, and because mass is large, the de Broglie wavelength is short, being on the order of 0.1 nm. Moreover, because the atoms are electrically neutral, this type of beam is not affected by the focusing limit due to the spatial charge effect, which is an essential problem in the case of charged-particle beams. We developed a novel lithography technique using a well-controlled metastable helium atom beam as the exposure source and a self-assembled monolayer as an ultra-thin resist in place

of the conventional thick resist. We have advanced this technology to the practical stage of processing semiconductors without using the conventional intermediate metallic thin layer.

As shown in Fig. 1, a resist is realized by removing the surface oxide layer from the Si (111) substrate which is to be processed, performing hydrogen termination, and then directly forming a self-assembled monolayer (SAM) on the surface by aligning silane molecules ( $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$ , OTS). A metastable helium atom beam with a slow thermal speed irradiates this monolayer resist through a stencil mask in vacuum. By etching the irradiated sample with an alkaline solvent, the pattern shown in Fig. 2 was formed. The dimensions of the pattern are  $5\mu\text{m}$ . However, the width of the step shown by the red in the graph at the right remains at 1-2 pixels, ach-

ieving an edge resolution of less than 100 nm.

The metastable atoms selectively extract electrons at the topmost surface, and trigger the cutting of bonds in the molecules and the crosslinking reaction. It is thought that differences occur in the etching resistance of the resist between the irradiated part and non-irradiated part as a result of this mechanism. However, a detailed elucidation, including achievement of higher resolution (10 nm level), is a subject for future research.

In addition to the above, NIMS is also involved in development of atomic and ionic quantum beams with controlled spin. Using this technology, we intend to clarify the spin behavior of topmost surface electrons under a strong magnetic field or in an element specific manner.

## Special Features

< Continued from p.1

### Quantum Beam Basic Technologies for Creation/Characterization of Nanomaterials

The activities of the Center's groups are summarized in the following: (1) The Synchrotron X-Ray Group is engaged in advanced characterization of nanomaterials using brilliant synchrotron radiation at KEK-PF (High Energy Accelerator Research Organization/Photon Factory), SPring-8 (large-scale synchrotron facility), etc. In particular, this Group's work includes research and development related to a new type of reflectometry which enables high resolution, real-time analysis of nanostructures such as "buried" interfaces, as well as precise structural analysis and a new photoelectron spectroscopy method utilizing the NIMS beamline at SPring-8. (2) The Neutron Scattering Group is developing new analytical software for neutron/X-ray scattering and multi-scale characterization methods by the small angle scattering technique using the neutron source JRR-3M (Japan Research Reactor-3M) and J-PARC (Japan Proton Accelerator Research Complex) as well as laboratory-level small angle scattering using X-ray sources. The Group is also involved in the creation of novel magnetic nanoparticle materials, superconducting materials, etc. using these technolo-

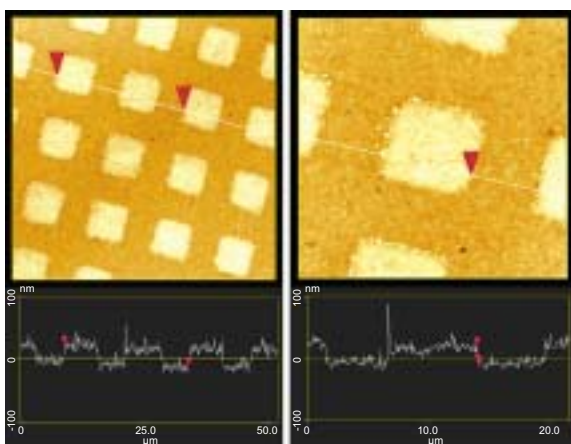
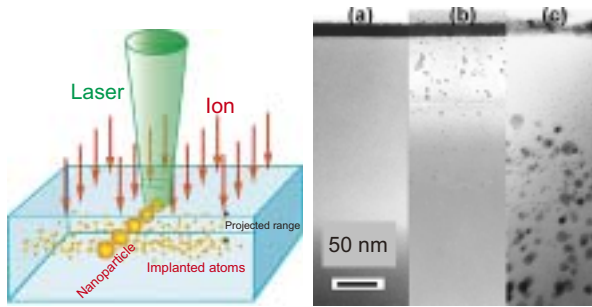


Fig. 2 Atomic force microscope (AFM) image of an Si (111) substrate processed by atom beam lithography.

## Development of Nanomaterials Using Ion Beam Technology

Naoki Kishimoto, Hiroshi Amekura  
Keiji Oyoshi, Yoshihiko Takeda  
Kenichiro Kono  
Ion Beam Group  
Quantum Beam Center (QBC)



**Fig. 1** Control of nanoparticle formation by ion and laser-ion co-irradiation. (a) Ion irradiation only, (b) sequential ion-laser irradiation, (c) Co-irradiation with ion and laser.

Remarkable nanoparticle precipitation occurs with laser-ion co-irradiation. Because this occurs only under the condition of ion-laser co-irradiation, the spatial distribution of the nanoparticles can be controlled by laser lithography.

Ion beam technology plays a key role in the semiconductor industry and has developed as a tool which makes it possible to introduce impurity atoms at specified depths in order to modify optical and electronic properties of semiconductor materials. On the other hand, because the development of device fabrication technology is largely dependent on microfabrication techniques, device fabrication has pushed forward in miniaturization toward the nano level using so-called top-down techniques such as lithography. Thus, the remarkable flowering of modern electronics has been realized based on a combination of ion beam technology and microfabrication techniques. In spite of these achievements, current electronic devices are reaching their theoretical performance limits, and from the technical viewpoint, micro/nanofabrication is also expected to reach its limits sooner or later. Hence, novel nanomaterial fabrication and control techniques are desired. In particular, precision 3-dimensional nano-control technology as an innovation for next-generation devices is considered the

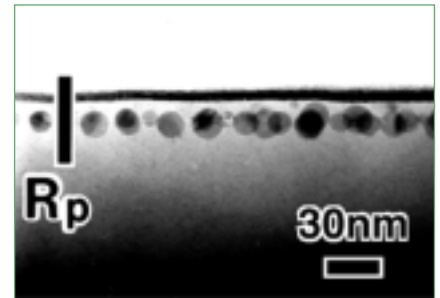
most critical development target. The Ion Beam Group is engaged in research and development utilizing the distinctive features of ion beam technology, namely, (1) high spatial controllability, which makes it possible to implant a variety of atoms at a specified depth in materials, (2) compositional control of materials using high flux ions, and (3) atomic transfer and radiation-induced reaction by electronic excitation and other techniques. Because the negative ion implantation method makes it possible to introduce arbitrary elements into transparent insulators, surface plasmon resonance energy can be controlled freely from the infrared region, which is important in current optical telecommunications, up to the visible range, which is expected to be key to next-generation applications. In particular, using the laser-ion co-irradiation technique to control nanoparticles (Fig. 1), which takes advantage of the dynamic synergistic effect of heavy ions and laser irradiation, as well as *in-situ* characterization and other techniques, the Group succeeded in creating a nanoparticle material for use in ultra-fast optical telecommunications with sub-picosecond response (Fig. 2) and operating energy tuning for a wide optical wavelength region (Fig. 3). As seen in these recent achievements, the Group is accumulating original technologies which will serve as a starting point for 3-dimension-

most critical development target.

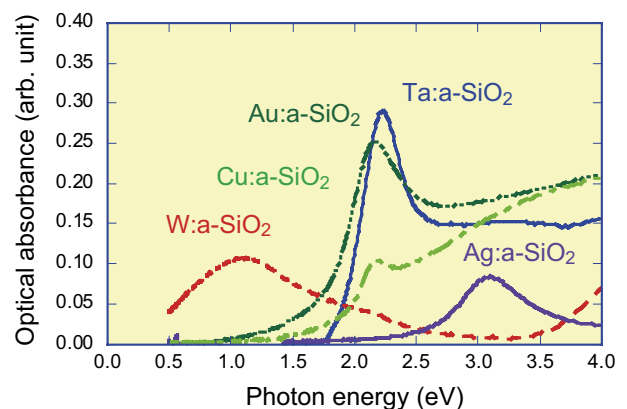
The Ion Beam Group is engaged in research and development utilizing the distinctive features of ion beam technology, namely, (1) high spatial controllability, which makes it possible to implant a variety of atoms at a specified depth in materials, (2) compositional control of materials using high flux ions, and (3) atomic transfer and radiation-induced reaction by electronic excitation and other techniques. Because the negative ion implantation method makes it possible to introduce arbitrary elements into transparent insulators, surface plasmon resonance energy can be controlled freely from the infrared region, which is important in current optical telecommunications, up to the visible range, which is expected to be key to next-generation applications. In particular, using the laser-ion co-irradiation technique to control nanoparticles (Fig. 1), which takes advantage of the dynamic synergistic effect of heavy ions and laser irradiation, as well as *in-situ* characterization and other techniques, the Group succeeded in creating a nanoparticle material for use in ultra-fast optical telecommunications with sub-picosecond response (Fig. 2) and operating energy tuning for a wide optical wavelength region (Fig. 3). As seen in these recent achievements, the Group is accumulating original technologies which will serve as a starting point for 3-dimension-

al nanostructural control.

The Ion Beam Group's future objectives include the development of a nanopatterning technology using ion beam projection as an ultimate technology for the direct production of 3-dimensionally controlled nanostructures in substrate materials with ultra-high accuracy and high throughputs. In outline, this is a technology for direct ion projection using an electromagnetic lens to project an ion beam pattern passed through a nano-patterned stencil. Using this approach, the Group is engaged in the development of the basic technologies for creation and characterization of nanomaterials using advanced ion beam technologies.



**Fig. 2** Transmission electron microscope (TEM) image of the cross section of silica glass with high-flux Cu ion implantation. Self-assembly of spherical metallic Cu particles with diameters of 10 nm occurs at a certain ion current density; these are arranged 2-dimensionally at positions somewhat shallower than the penetration range,  $R_p$ , of the ions. (The black horizontal line is the surface marker Cr film.)



**Fig. 3** Optical absorbance spectrum of various metallic nanoparticle-dispersed materials formed by the high-flux negative ion implantation technique. The absorbance peaks, which change depending on the ion species, are due to surface plasmon resonance. The materials show ultra-fast nonlinear optical characteristics at the sub-picosecond level.

gies. (3) The Ion Beam Group is engaged in the creation of nano-quantum materials by the laser-ion co-irradiation method using EPF (Extreme Particle Field generator) and the ion projection method. (4) The Atomic Beam Group is conducting research and development on nanopatterning technology by atomic beam lithography, etc.

The aim of the Quantum Beam Center is to develop basic technologies which will make a significant contribution to the creation of nanomaterials by comprehensive use of these quantum beam technologies.



# Development of Nanomaterials Using Neutron Beam Technology - Observing Objects with Neutrons -

Hideaki Kitazawa, Masato Ohnuma  
 Fujio Izumi, Masashi Hase  
 Hiroyuki Suzuki, Hiroaki Mamiya  
 Naohito Tsuji, Seiichi Kato, Shigenori Ueda  
 Neutron Scattering Group  
 Quantum Beam Center (QBC)

As neutrons are particles which possess spin but have no electrical charge, a precise investigation of the spatial positioning of the nuclei of the atoms making up substances, the spin state of electrons and other phenomena is possible using neutrons. In the Neutron Scattering Group, our objective is to create the innovative new functional materials which will be essential for realizing a next-generation IT society and low environmental load society by utilizing the precise crystal structure characterization technology for X-ray and neutron powder diffraction, small angle X-ray/neutron scattering technology and nano-quantum material creation technology cultivated to date, and achieving higher levels in these technologies.

Concretely, using neutrons and synchrotron radiation, we are conducting multi-scale characterizations from the atomic size (crystal/magnetic structure, etc.) up to the macro scale level (fine texture, etc.) of (1) nanocomposite materials such as magnetic nanogranular materials and structural materials and (2) high efficiency energy conversion materials such as magnetic refrigerator materials, superconductors, and cell materials, among others. Characterization of special sizes in hierarchical structures, elucidation of electronic states in magnetism and superconductivity, clarification of the migration paths of defects and mobile atoms, and similar research are expected to lead to innovative advances in materials and the creation of novel materi-

als.

For example, Co-Pd-Si-O nanogranular soft magnetic material is a material with a fine structure in which Co or other magnetic particles with a particle size of several nm are embedded in an oxide phase. Because this material has large electrical resistance, large saturation magnetization, and large induced magnetic anisotropy, it is expected to find use in the gigahertz region, which will become important for realizing higher density and higher speed in information transmissions. We are carrying out research using the small angle neutron scattering method in order to identify the ultimate cause of the large induced magnetic anisotropy in this material. In small angle neutron scattering, the largest contribution of magnetic scattering, and hence the maximum scattering intensity, occur when the local magnetic moment and scattering vector form a 90° angle. However, contrary to expectations, in the nanogranular soft magnetic material, the maximum intensity appears in the direction parallel to the direction of easy magnetization in which local magnetization is oriented (see figure). Based on this fact, it is clear that there is also an accompanying magnetization component which is rotated 90° to the main magnetic orientation. Fur-

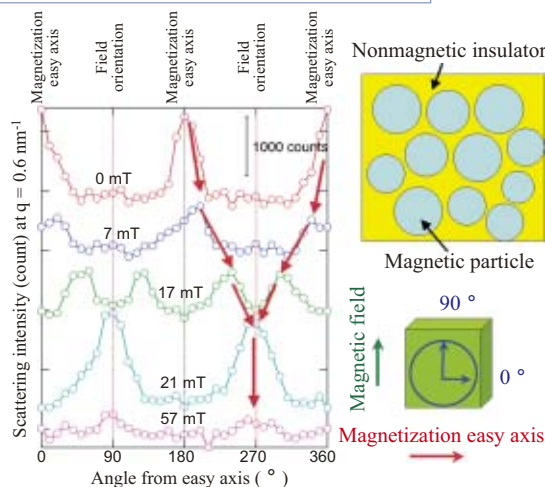


Fig. Field orientation dependence of neutron scattering intensity. The wavenumber  $q = 0.6 \text{ nm}^{-1}$  corresponds to a structure on the order of approximately 10 nm in real space.  $0^\circ$ ,  $180^\circ$ , and  $360^\circ$  are the orientations of the axes of easy magnetization.

thermore, when an external magnetic field is applied, this 90° component rotates together with the main magnetic component, and in the vicinity of 21 mT (magnetic anisotropy field), where the main magnetization component is substantially aligned with the external field orientation, a peak of scattering intensity in the direction parallel to this appears once again. Because these idiosyncratic magnetization behaviors are considered to hold the key to the manifestation of the large anisotropy field in the nanogranular material, we are now carrying out more detailed research jointly with the Research Institute for Electric and Magnetic Materials and the Japan Atomic Energy Agency (JAEA).

## NIMS News

### Visit by Czech Universities Rectors and Conclusion of MOU



(October 31, NIMS) -- Prof. Václav Hampl, Rector of Charles University, and Prof. Jiří Málek, Rector of the University of Pardubice, both in the Czech Republic, visited NIMS to discuss collaboration with President Teruo Kishi of NIMS and Dr. Hajime Haneda, Managing Director of Sensor Materials Center. As NIMS and Charles University are already cooperating



From the left: Prof. Hampl, Prof. Málek, Prof. Kishi, Dr. Haneda, Dr. Murase, ICYS, Dr. Mitsuhashi, ICYS, and Dr. Kanda, NIMS International Affairs & Public Relations Office.



Prof. Hampl and students of Charles University.

under the international joint graduate school program, Prof. Hampl held an informal discussion with five Charles Univ. students who are currently studying at NIMS. Prof. Málek has had exchanges with NIMS and the former NIRIM (National Institute for Research in Inorganic Materials) for more than 10 years through joint research and other activities. During this visit, Prof. Málek and Dr. Haneda signed an MOU for joint research in R&D of advanced materials by the Faculty of Chemical Technology of the University of Pardubice and the Sensor Materials Center and International Center for Young Scientists (ICYS) on the NIMS side.

# Realtime Observation of Surfaces and Buried Interfaces of Thin Films and Multilayer Films

## - Development of Quick X-Ray Reflectometry -

X-ray reflectometry is a nondestructive technique to see the layered structures of thin films and multilayer films based on the optical total reflection phenomena of X-rays, and gives information of the density and thickness of each individual layer, roughness and

diffusion of individual interfaces, etc. The method, so far, has required some angular scans during the data collection, and this limits the scope of the research - only stable systems can be candidates to be studied. Recently we have succeeded in developing a novel technique,

Kenji Sakurai  
Synchrotron X-Ray Group  
Quantum Beam Center (QBC)

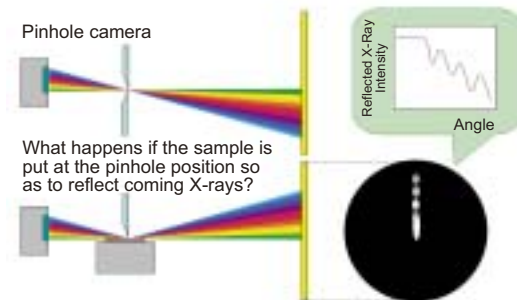


Fig. 1 Principle of quick X-ray reflectometry developed by NIMS (patented).

which permits the measurements without any scans, i.e., with absolutely no movement of the specimen and the optical system. As a result, it has now become possible to observe the surface and buried interfaces in ever-changing systems.

The principle of the quick X-ray reflectometry developed by the NIMS is shown schematically in Fig. 1. One would know that a pinhole camera produces an image on a screen. When the specimen is placed just at the position of the pinhole, each angular component of incident X-rays are reflected by the specimen because of the total reflection, and then goes to the screen. This indicates that one can get X-ray reflectivity profile simultaneously on the screen, and by just repeating the exposure and the read out, it is possible to track structural changes in the surface and interface as a function of any environmental parameters, such as temperature, pressure, light irradiation, etc.

critical angle. In this figure, one can see the critical angle changes greatly during changes of the temperature. Moreover, as described in the inset, even at the same temperature, the critical angle does not agree in the cooling and heating runs, resulting in some hysteresis. This suggests emerging and vanishing of thin additional layers with very different density, and is interesting from a viewpoint of the changes of physical properties during the phase transition, such as switching between hydrophobic and hydrophilic natures of the thin film.

The Synchrotron X-Ray Group will continue the instrumentation for this new experimental method, quick X-ray reflectometry, and will also try the realtime observation of the surfaces and buried interfaces of many interesting ever-changing systems which have been difficult to study until now.

Fig. 2 shows one typical example of quick X-ray reflectometry. A measured sample is a temperature-responsive polymer thin film prepared on a silicon substrate. Generally X-ray reflectivity decreases abruptly at the specific position called the

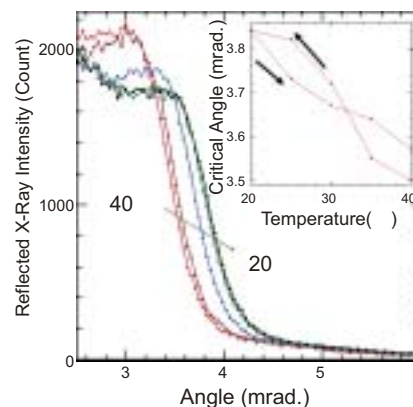


Fig. 2 X-ray reflectivity of temperature-responsive polymer thin film.

## NIMS News

### 4th Japan-Sweden Bio-Nanotechnology Workshop was Held at NIMS



(November 13-15, NIMS) -- The 4th Japan-Sweden Bio-Nanotechnology Workshop was held, sponsored jointly by Japan's Ministry of Education, Culture, Sports, Science and Technology (MEXT) and the Swedish Foundation for Strategic Research. This Workshop is held alternately in Sweden and Japan and the recent event was the 4th in the series.

Several renowned researchers in bio-nanotechnology attended, including Prof. Masuo Aizawa, President of Tokyo Institute of Technology, from Japan and Prof. Thomas Laurell of Lund University from Sweden. The workshop featured lectures in seven sessions, including nano-bioelectronics, cell and bio-molecule manipulation and analysis using chips, medical applications of biotechnology, nanoscience and nanomaterials for biotechnology, etc., and 35 presentations on new research, including poster presentations by eight young researchers on the Japanese side. The event was characterized by spirited debate. Following the workshop, tours of nano- and bio-related laboratories at NIMS were held on November 15.



A scene at the workshop.

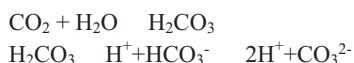
## Process for Simultaneous CO<sub>2</sub> Reduction and H<sub>2</sub> Production

### - Environmental and Energy Countermeasures Utilizing Scrap Iron -

Hiroimi Eba  
Synchrotron X-Ray Group  
Quantum Beam Center (QBC)

There are probably many people in Japan who begin using disposable "pocket warmers" before real winter weather. These pocket warmers are a cheap, convenient product which takes advantage of the fact that iron rusts easily, in other words, oxidizes, and generates heat in the process. Because the objective of the research introduced in this article is to prevent global warming by reducing carbon dioxide (CO<sub>2</sub>), this discussion of pocket warmers - which produce heat - may seem to be headed in exactly the wrong direction, but in fact, we found that it is possible to capture CO<sub>2</sub> using the same oxidation reaction of iron as that in the pocket warmer.

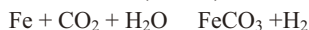
First, CO<sub>2</sub> is dissolved in water. This produces the same carbonated water as in soda water or beer.



An oxidation-reduction reaction occurs when iron (Fe) is reacted with these hydrogen ions (H<sup>+</sup>):



Therefore, when this is combined with the first equation, as shown below, iron carbonate (FeCO<sub>3</sub>) is formed:



From this equation, it can be understood that CO<sub>2</sub> can be absorbed and fixed using the oxidation reaction of iron, and at

the same time, hydrogen gas (H<sub>2</sub>) is also liberated.

The reaction expressed by the above equation was confirmed experimentally. The iron was powdered to enhance reactivity and reacted with CO<sub>2</sub> and water at room temperature. The figure shows the results of an analysis of the change over time in the gas concentration in the reaction vessel. It can be understood that the concentration of CO<sub>2</sub> was reduced by half in approximately 15 minutes, and in place of this, the same volume of H<sub>2</sub> was generated. Ultimately, 100 % of the CO<sub>2</sub> was absorbed and iron carbonate powder was recovered. Iron carbonate is a species of iron ore, called siderite, which occurs in nature. With this reaction, it is possible to absorb approximately 450 L (790 g) of CO<sub>2</sub> per kg of iron, which is a high absorption rate in comparison with many of the absorbents which are currently used. Likewise, high expectations can be placed on this process as a hydrogen production method, as there are virtually no existing technologies which are capable of producing H<sub>2</sub> at room temperature and the process produces approximately 450 L (36 g) of H<sub>2</sub> per kg of Fe. These results suggest that this method

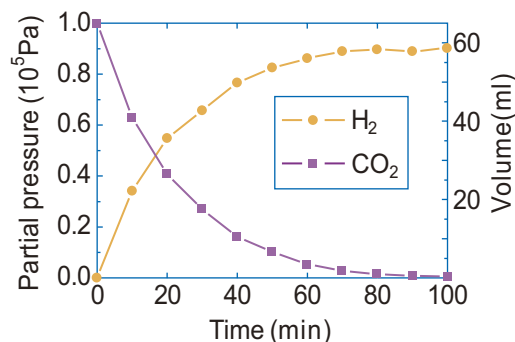


Fig. 1 Decrease in CO<sub>2</sub> and increase in H<sub>2</sub> with time during iron carbonation reaction. (0.4 g of Fe, CO<sub>2</sub> at 1 x 10<sup>5</sup> Pa (atmospheric pressure) and 2 ml of water were reacted in container with a volume of 65 ml.)

is compact and safe in comparison with the hydrogen tanks which can be used today, and correspond to a larger amount of hydrogen containment per unit of mass than with hydrogen storage alloys.

Iron is widely used as a material in steel, stainless steel, and other forms. However, because huge amounts of scrap iron are currently generated in Japan, recycling has become difficult. If this scrap can be used as a raw material for this process, it will be possible to implement an urgently-needed reduction in CO<sub>2</sub> emissions and supply H<sub>2</sub> as a new form of energy which will enjoy expanded demand in the future, and to accomplish this using waste. This is expected to have a large ripple effect on both industry and society.

## Materials Science Research Using Synchrotron Radiation

### - High Energy Photoelectron Spectroscopy and Materials Science -

Keisuke Kobayashi, Hideki Yoshikawa  
Masahiko Tanaka  
Synchrotron X-Ray Group (SPring-8)  
Quantum Beam Center

NIMS possesses a dedicated undulator beamline, BL15XU, which is part of the large-scale synchrotron radiation facility SPring-8 and boasts the world's largest size and highest performance. This undulator beamline has the unprecedented feature of covering a wide region from soft X-rays to 20 keV hard X-rays. High energy resolution, high energy photoelectron spectroscopy utilizing this feature was introduced at the NIMS BL15XU dedicated beamline, creating a system for powerfully promoting research for materials science.

Silicon LSIs were formerly produced using only an extremely small number of materials, which included Si substrate, polycrystalline Si, SiO<sub>2</sub>, Al, and certain others. Today, however, diverse materials are used. For example, high permittivity materials such as SiON, HfO<sub>2</sub>, etc. are used in gate insulation films, metallic silicide and transition metals such as W and Mo are used in gate electrodes, and Cu

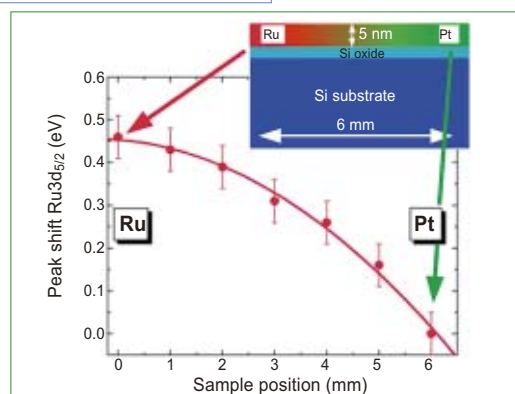


Fig. 1 Value of band offset of SiO<sub>2</sub> interface with an RuPt alloy electrode having a gradient composition of SiO<sub>2</sub>/Si obtained as the value of the shift in the Ru 3d<sub>5/2</sub> photoelectron peak. As X-ray energy, 4.75 keV was used.



## Advanced Crystal Analysis Using Synchrotron Radiation

Akiji Yamamoto, Masahiko Tanaka  
Yuichi Michiue, Hiromoto Nakazawa  
Synchrotron X-Ray Group (Spring-8)  
Quantum Beam Center (QBC)

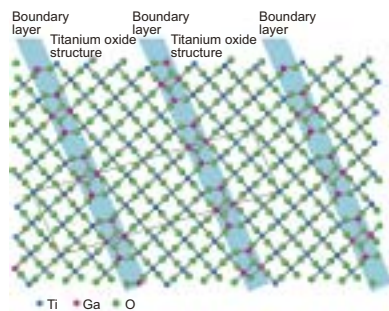


Fig. 1 Crystals structure of  $Ga_4Ti_{m-4}O_{2m-2}$  ( $m = 17$ ). The boundary layer spacing is approximately 1.7 nm.

Precise, atomic-level structural data (fractional coordinates, interatomic distance, etc.) is one critical type of information which is most basic for evaluating and predicting the properties of materials. Crystal structure analysis using X-ray diffraction (X-ray crystal structure analysis) is an effective means of obtaining this information, but there are naturally various restrictions and limitations on its application. To overcome these difficulties, it is considered necessary to achieve advances in both measurement (device development) and analysis (development of new methodologies and programs).

We developed the world's

highest level high resolution X-ray diffractometer at the NIMS dedicated beamline, BL-15XU, which is installed at the Spring-8 synchrotron radiation facility, and are working to realize even higher functions in this device. Recently, we also succeeded in constructing a high speed, high accuracy data collection system

which possesses both high angular resolution and high efficiency by introducing a camera of a large-radius. Where analytical techniques are concerned, we have grappled with the establishment of higher-dimensional crystallography (crystallography which treats structures embedded in spaces of 4 or more dimensions) and the development of programs for the primary purpose of dealing with aperiodic crystals such as quasicrystals. We also devised a systematic method for analyses of long-period structures applying the same principle. By combining these kinds of advanced measurement devices and analytical techniques, we aim to de-

termine complicated crystal structures, which had been difficult with conventional methods, and also enable quicker, more precise analysis of materials.

$Ga_4Ti_{m-4}O_{2m-2}$  (Fig. 1), which we recently analyzed, can be regarded as a type of superlattice in which gallium oxide ( $-Ga_2O_3$ ) type boundary layers are introduced into the structure of titanium oxide. The symmetry of this kind of structure is low, and in addition, it has a long period exceeding several nanometers. In analyses of this kind of long-period crystal, growth of high quality single crystals for use in diffraction measurements had been considered indispensable. However, by performing data measurements with the BL-15XU high resolution X-ray diffractometer (Fig. 2) and analyzing this sample as a kind of modulated structure using the principle of higher-dimensional crystallography, we demonstrat-

ed that it is possible to obtain structural data with high accuracy by the powder diffraction method. In the future, we hope to contribute to development of the X-ray structural analysis technique as a basic technology for nanoscience by promoting advanced research and development from the directions of both measurement and analysis.

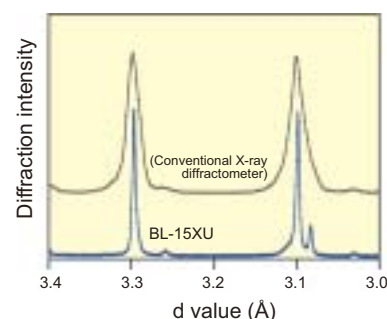


Fig. 2 Comparison of profiles (partial excerpt only) of a powder specimen of  $Ga_4Ti_{m-4}O_{2m-2}$  ( $m = 17$ ) using the BL-15XU high resolution X-ray diffractometer and a conventional X-ray diffractometer. In the former, two peaks in the vicinity of  $d = 3.1 \text{ \AA}$  are clearly separated.

is used in wiring. TaN and other nitrides are used in Cu diffusion barriers, and low permittivity films are used as interlayer insulating films in multilayer wiring. Thus, many kinds of nano-functional thin films are necessary in today's device development, as represented by those mentioned above.

In the development of nano-scale multilayer thin film materials, techniques for investigating the electronic state and chemical bonding condition of the thin film and reactions and interdiffusion at interfaces become necessary. Photoelectron spectroscopy (PES) is one essential technique for investigations of this type. However, as a drawback of conventional PES, because this method used low energy X-ray, it was overly sensitive to the atomic-scale surface layer, making it impossible to observe the interiors of substances. If the kinetic energy of the photoelectrons can be increased, this drawback can be overcome. Therefore, a high energy PES technique for

observation of the interior of substances has been strongly desired for use in analyses of practical devices. For example, as shown in Fig. 1, it is possible to measure the band offset of the SiO<sub>2</sub> interface with an alloy electrode with a 5 nm thick gradient composition by PES using a 4.75 keV X-ray. Band offset is an important physical property which controls the characteristics of semiconductor devices. If the excitation energy can be increased further, to the harder X-ray region, PES of nano-thin films of 5-10 nm or more will become possible, enabling analysis of practical devices having more complex multilayer structures. At the NIMS beamline, we

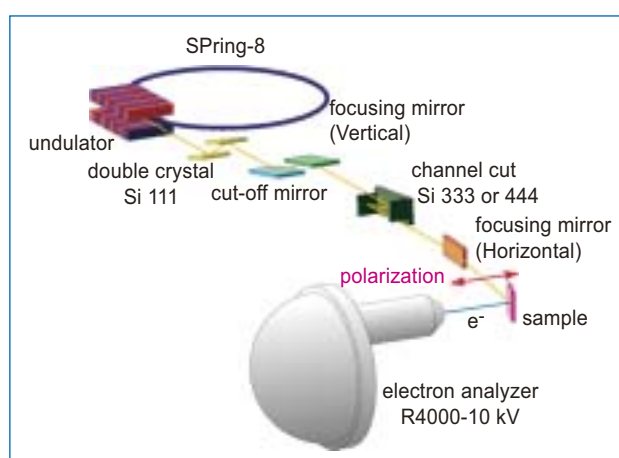
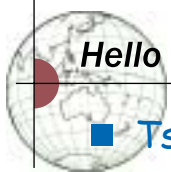


Fig. 2 Hard X-ray photoelectron spectrometry characterization system.

are constructing a higher energy resolution, high throughput system for this purpose, as shown in Fig. 2, and expect to begin operation within this year.



## Hello from NIMS

### ■ Tsukuba is Wonderful ■

I have worked in NIMS for 8 months. My research and life here are unforgettable.

I enjoy life in Tsukuba Science City. Frankly speaking, it is even better than I had imagined before I came here. Tsukuba people are kind and friendly, so we newcomers all have a nice feeling and want to become part of Tsukuba society.

I am working in the Biomaterials Center at the Namiki Site. My work is related to the synthesis of calcium phosphate/collagen nanocomposites as bone replacement materials. It is interesting work. I am gradually learning to work properly, collaborate with my officemates compatibly, and explore my study independently.

Tsukuba is beautiful. It is precious to find a young city that always gives people a feeling that it has been immersed in and accumulating culture for a long time. Whatever the ancient mystery and dignity or the modern prosperity, you can have a spot of it on such occasions from time to time. I wish Tsukuba and NIMS a bright tomorrow!

Dandan Sun (University of Sydney, Australia)  
International Joint Graduate School Program (February 2006-January 2007)  
Nano-Structured Biomaterials Group  
Biomaterials Center



[ From a trip to Kansai with Charles University students (first from left) ]

# nims ILLUMINATION

-Let's draw big pictures in a night sky-  
December 7-25, 2006



-Illumination Making by elementary students-  
December 4, 2006



-Year of the Boar 2007-  
January 1-7, 2007



PUBLISHER  
Dr. Hisao Kanda

### To subscribe, contact:

Ms. Naoko Ichihara  
International Affairs &  
Public Relations Office, NIMS  
1-2-1 Sengen, Tsukuba, Ibaraki  
305-0047 JAPAN  
Phone: +81-29-859-2026  
Fax: +81-29-859-2017  
inquiry@nims.go.jp

NIMS NOW International is a monthly newsletter made for international readers to introduce our latest research activities and events.

Our official website provides you with the back issue download as well as the news on most recent activities at

<http://www.nims.go.jp/>