from Tsukuba, Japan to the world

NIMS NOW

National Institute for Materials Science

Vol.2 No.6 April, 2004

RESEARCH FRONTIER

In-situ formed two phase metallic glass with surface fractal microstructure

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Metallic glasses with better glass forming ability have been sought for many years since its discovery in the 1960's. According to Turnbull, glass formation is favored in alloys with a high reduced glass transition temperature, $T_{rg} = T_g/T_l$, where T_g is the glass transition temperature and T_l is the liquidus temperature. The nucleation of crystals can be suppressed more easily in this condition during quenching due to the combination of a lower driving force for nucleation and a lower mobility in the melt. Indeed, well known good metallic glass formers have compositions which are close to the deep eutectics in multi-component systems that are composed of elements with high negative heats of mixing for all possible combinations. Consequently, the elements mix homogeneously with nearly dense packing configuration in a deep eutectic. Thus, phase separation in a melt is not possible in binary metallic glasses. However, phase separation may be possible in multicomponent metallic glasses, if the values of the negative heats of mixing differ. Several claims have been made on phase separation in bulk metallic glasses. However, since the tendency of phase separation makes the glass unstable, it has been difficult to detect a phase separated microstructure in metallic glasses, although such microstructures have been commonly observed in oxide glasses. < Continued on p.4

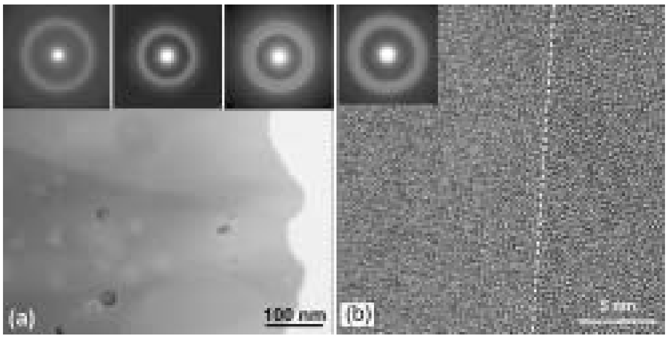

Fig. (b) TEM bright field image and (b) HREM image of a $La_{27.5}Zr_{27.5}Al_{25}Cu_{10}Ni_{10}$ two phase metallic glass. Two types of halo rings corresponding to different average atomic distances are observed in (a). When selected area aperture covers two phase, two halo rings are observed in one selected area electron diffraction pattern. HREM image shows two phases are fully amorphous with only difference in average atomic distance, namely, composition.

In this issue

NIMS NEWS

Visit by Students from Switzerland's EPFL

On February 24, NIMS received a visit from Prof. Hoffmann and about 20 students from the Swiss Federal Institute of Technology Lausanne (EPFL). The students toured various facilities at the Sengen Site, including the Metallic Nanostructures Group and High Temperature Materials Group in the Materials Engineering Laboratory (MEL) and the Reconstitution Materials Group in the Biomaterials Center (BMC). The visitors viewed the laboratories and experimental equipment with great enthusiasm.

Research and Development of High-Energy X-Ray Photoelectron Emission Microscope

—A New Tool that Exceeds the Limits of Surface Analysis—

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In front-line material development, requirements for a shorter time scale in the process from new material synthesis to analysis and practical application have become increasingly strong in recent years, while analysis performance must satisfy the mutually contradictory needs of easy data analysis and higher accuracy. Progress from these viewpoints is also expected in photoelectron spectroscopy, which is used to identify the chemical bonding and electronic states of solids. Photoelectron spectroscopy is a technique for investigating the electrons discharged by light irradiation. However, ambiguity or confusion may occur in some cases because (1) observation of the ultramicroscopic region is not a strength of this method and (2) surface reactions of the sample in air cannot be ignored due to the high sensitivity of the surface layer at nano metered level thicknesses.

Fig. 1 Revolver switching-type undulator X-ray source.

The photoelectron emission microscope using high-energy X-ray overcomes these problems because (1) observation of ultramicroscopic regions in the specimen surface direction is possible by employing emission microscope technology and (2) observation of a deep layer exceeding 10 nm from the surface is possible by using high energy X-rays (several keV or higher). As a light source, the world's most brilliant X-ray source at the synchrotron radiation facility SPring-8 is used in the NIMS dedicated beamline BL15 (see **Fig. 1** and **Fig. 2**).

By utilizing a method of detecting all photoelectrons, a spatial resolution of 30 nm has been realized with the device in **Fig. 3**. Taking advantage of the strengths of synchrotron radiation, which makes it possible to control X-ray energy, we have also succeeded in obtaining X-ray absorption spectrum images which include information on the unoccupied states of electrons in solids. **Fig. 4** shows a photoelectron emission microscope image of an array of Ag dots fabricated on a Si substrate by lithography and the X-ray absorption spectrum from one dot. Because high expectations are placed on Ag microdots as a system of optical memory elements which exceeds the wavelength limitations of light, development of a Ag and its oxide-growing technology is important. Changes in chemical state during the oxidation process can be clearly grasped in the micro region by observing the spectrum change from the red line to the blue in **Fig. 4**.

The photoelectron emission microscope using high-energy X-ray excitation cannot be categorized as a conventional surface analysis technique. This new technology is expected to be developed as a precise chemical state characterization method for 3-dimensional spaces.

Fig. 2 Linear polarized light from undulator observed with fluorescent plate (20 x 20 mm).

Fig. 3 Photoelectron microscope in beamline hatch.

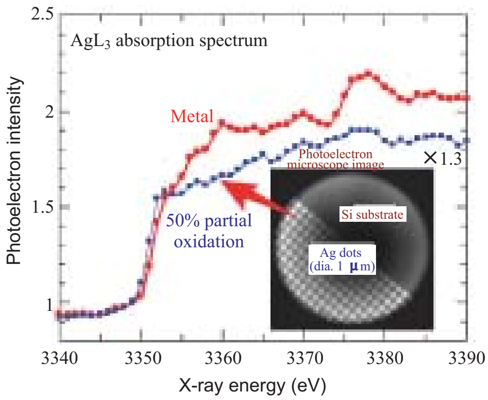

Fig. 4 Photoelectron microscope image of Ag dot array and X-ray absorption spectrum obtained from 1 dot.

Visit by China's Vice Minister of Science and Technology

On February 4, NIMS was honored with a visit by Prof. Jin-Pei Cheng, Vice Minister of Science and Technology of China, and several other officials from the Ministry and the Chinese Embassy in Japan. After a briefing on NIMS' management strategy, the guests inspected the research sites of the Biomaterials Center, Metallic Nanostructure Group (Materials Engineering Laboratory), and Electro-nanocharacterization Group (Nanomaterials Laboratory). Chinese researchers account for approximately 1/3 of all foreign researchers at NIMS and are one of the Institute's valuable assets. Following this visit, additional cooperative relationships with leading research institutes in China are anticipated.

State Analysis and Nanotechnology Support

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A main direction in advanced research on analysis technologies is developmental research on physical property analysis methods for the ultramicroscopic region approaching the electron order. One subject of work at the NIMS dedicated beamline (SPring-8 BL15XU) is research based on sound early forecasts of technologies which will become the mainstream, such as the photoelectron microscope introduced in this issue. While we carefully follow these new trends, on the other hand, in an increasing number of cases, we are also keenly aware of the importance of accurately analyzing the average electron state of materials as a whole. The following presents a typical example of this in our general support program for nanotechnology.

Fe_2O_3 and $FeTiO_3$ are each well-known substances. Although both are semi-ferromagnetic insulators, solid solution Fe_2O_3-$FeTiO_3$ is a semiconductor which displays ferrimagnetism and thus has great promise as an environment-friendly material for spintronics. We analyzed the chemical state of this substance, particularly with respect to Ti, in response to a request from a group headed by Asst. Prof. Tatsuo Fujii of Okayama University. While the electronic state of Fe can be analyzed reliably by Mossbauer spectrometry, virtually no practical method is available for Ti, and especially for Ti oxide powders. To solve this problem, at the beamline, we first made high resolution measurements of designated X-rays of Ti with powder samples of TiO_2, TiO_3, and $FeTiO_3$ in order to obtain state standards for Ti (joint work with Asst. Prof. Yoshiaki Ito, Kyoto University, a NIMS guest researcher). As an example, **Fig. 1** shows a high resolution Ti Kα spectrum of $FeTiO_3$. Here, we were surprised to see that Ti in $FeTiO_3$ apparently does not assume the same state (tetravalent) as in TiO_3, but rather, is close to the state (trivalent) in Ti_2O_3. On the other hand, because these oxide specimens were powders, it was nearly impossible to eliminate surface contamination, and analysis by ordinary X-ray photoelectron spectroscopy (XPS) was extremely difficult. This problem was solved with the NIMS dedicated beamline, as the influence of surface contaminants can be effectively eliminated by using a higher excitation energy, making it possible to analyze even insulators in powder form. **Fig. 2** shows the measured results obtained by XPS with high energy excitation and clearly indicates that, in fact, the Ti in $FeTiO_3$ is not in the same state (tetravalent) as in TiO_2. Even though this may be considered common sense, it also demonstrates the importance of reliable confirmation when necessary.

This successful result with $FeTiO_3$ was presented in a 30-minute television program as an example of leading-edge nanotech research.

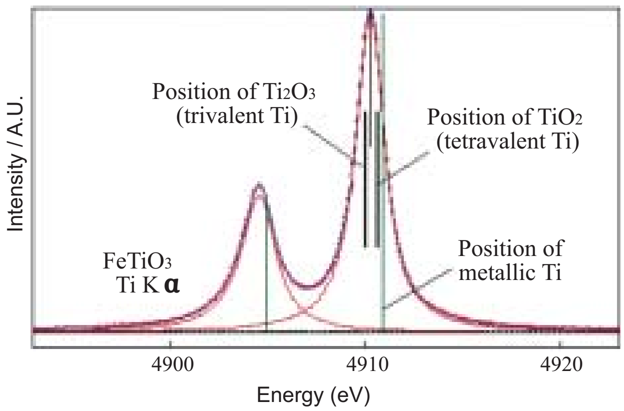

Fig. 1 Example of Ti spectrum obtained by high resolution X-ray spectroscopy.

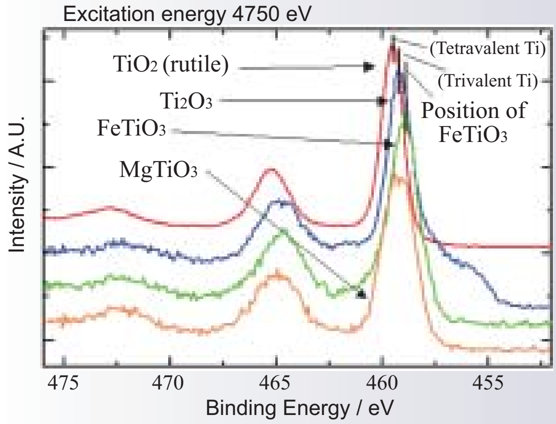

Fig. 2 Example of Ti spectrum by high energy excitation XPS.

For further information, please visit: http://www.nims.go.jp/abg/eng/index.html

JICA Trainee Researchers Visit NIMS

On February 12, five researchers in the JICA program at the National Institute of Advanced Industrial Science and Technology (AIST) visited the NIMS Namiki Site. The young researchers, who came from China, Mongolia, Panama, and Palestine, were given a brief presentation on NIMS, followed by a tour of the laboratories of the Advanced Beam Analysis Group and the High Pressure Group, both in the Advanced Materials Laboratory (AML). At the latter facility, the group saw a demonstration on research in diamond synthesis.

Meeting with the Press to Announce New Developments at Biomaterials Center

On February 13, NIMS held an informal meeting with the press from Tsukuba Science City at the NIMS Namiki Site to announce the progress of a cooperative system between the medical and engineering field and explain future efforts in this area. The new system will be implemented by the Biomaterials Center (BMC). The meeting also featured a lively exchange of opinions with newly-appointed Director Yoshiyuki Uchida of the Medical Applied Technology Group, who is a clinician on service. The Biomaterials Center intends to extend its work into medical applications by developing new biomaterials such as carriers for drug delivery systems (DDS).

Non-destructive Observation of "Buried" Interfaces

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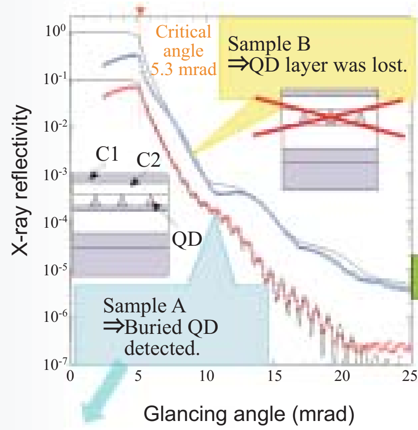
Materials Engineering Laboratory (MEL)

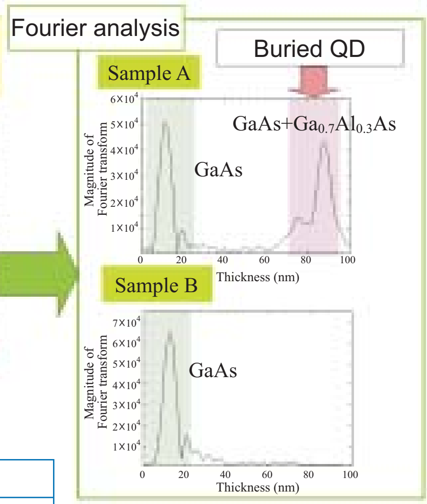
So far X-rays have been frequently used for seeing inside the materials because of the high transmission power. However, X-rays can be used for studying the surface and interfaces of thin films. When X-rays are irradiated on the flat, smooth surfaces at a small angle in the order of 0.1 deg, the total reflection takes place. The penetration depth then becomes extremely shallow, typically 1~100 nm near the critical angle, leading to the technique surface sensitive. Synchrotron radiation is an ideal source for the X-ray reflectometry (XR) experiments using total reflection this, because of its high brilliance.

The thin films used in many functional materials, such as semiconductors and magnetic materials, are one promising area for the XR investigation. For the most cases, the surface of the thin films is usually covered with a capping layer to protect from possible oxidation and any physical/chemical damages. Although it is crucial to check the structure of thin films after the deposition of capping layer, the analysis is not easy - almost all surface-sensitive methods are not available just because of this coverage of the surface. Therefore a non-destructive analysis of the "buried" interfaces is one of the increasing demands in modern nanotechnologies.

Fig. 1 shows the XR analysis of 'buried' GaAs quantum dots (QD) with capping layers. In this research, two specimens, produced under slightly different conditions, were studied. One can see a clear difference between the XR profile for specimens A and B; A exhibits short-period interference fringes corresponding to the existence of the QD layer, while B only has slow oscillation, which is due to capping layers. The data indicates that the QDs in specimen B are lost after the deposition of capping layers. As shown in **Fig. 1**, Fourier analysis of the XR data would be helpful in the interpretation. The method was proposed by X-Ray Physics Group for the first time in 1990.

We are currently engaged in extending XR - normal XR only measures specular reflectivity, but it is also important to see weak non-specular reflectivity to discuss the detailed structure of surface and 'buried' interfaces. Developing a new theory for model-free analysis is another significant task to apply the XR technique to more complicated 'buried' system.





Thickness of capping layer (C1, GaAs)	11 nm
Thickness of capping layer (C2, $Ga_{0.7}Al_{0.3}As$)	76 nm
Height of QD	17.5 nm
Number density of QD	1.6×10^{11} / cm^2

Fig. 1 Experimentally obtained X-ray reflectivity of GaAs quantum dot specimens A and B (left) and the Fourier analysis (right). The table shows the obtained parameters for D in specimen A. (The solid line in the left graph shows the calculated X-ray reflectivity using these parameters.).

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

< Continued from p.1

In-situ formed two phase metallic glass with surface fractal microstructure

To detect phase separation in a metallic glass, we have selected a system which includes one pair of elements with a positive heat of mixing to force phase separation, while having high negative heats of mixing with the other elements for glass formation. A two-phase metallic glass was then successfuly fabricated in an alloy composition with a mixture of two good glass forming alloys, La-Al-Cu-Ni and Zr-Al-Cu-Ni. The heat of mixing of La and Zr is positive, while both elements have negative heats of mixing with the other three elements Al, Cu and Ni. A two phase metallic glass with a surface fractal microstructure was obtained by melt-spinning the $La_{27.5}Zr_{27.5}Al_{25}Cu_{10}Ni_{10}$ alloy. This alloy phase separates into (La-Cu)-rich and (Zr-Ni)-rich glassy phases during quenching from the melt. The as-quenched samples consist of two amorphous phases that have a spherical shape with a wide range of length scales from tens of micrometers to a few nanometers. Some of them were fibers elongated along the direction of the melt-spun ribbon. Several identical generations of spheres in spheres were observed using scanning electron microscopy and transmission electron microscopy. Small angle x-ray scattering results show an exponential dependence to the power of -3.4 of intensity on the scattering vector, indicating a surface fractal microstructure of dimension 2.6. The selected area diffraction patterns that were obtained from the two-phase regions show two clearly distinguishable halo rings, and the high resolution electron microscope image shows isotropic maze patterns with two different length scales corresponding to the difference in the average atomic distance of the two amorphous phases.

[This result will be published in *Acta Materialia*, Vol. 52. The link to the paper is http://dx.doi.org/10.1016/j.actamat.2004.01.036]

For more information, visit the following web site: http://www.nims.go.jp/apfim/

Material Development using Novel X-Ray Fluorescence (XRF) Technique

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Materials Engineering Laboratory (MEL)

X-ray fluorescence (XRF) analysis has long been used in studying cultural treasures, analyzing environmental samples, and controlling industrial products. To enable more effective and informative use of XRF in material analysis, the X-Ray Physics Group developed an XRF imaging technique based on a new principle, which makes it possible to display the chemical composition and distribution of materials on a computer screen. Conventionally, a similar imaging required several hours to an entire day, even with synchrotron radiation. The new technology now enables ultra-high speed imaging in 0.1 to several seconds.

We are using this technology not only in material analysis, but also in new material development. Specifically, the new method is proving extremely useful when applied in combination with the combinatorial material synthesis process developed in recent years. The combinatorial process enable efficient, labor-saving material development by fabricating multiple heterogeneous materials simultaneously on a single substrate. XRF imaging of the substrate enhances the advantages of this process by making it possible to evaluate multiple materials simultaneously. **Fig. 1** shows a combinatorial specimen using composition as a parameter. From this image, it can be understood that the manganese content is higher in the lower materials. Using numerical analysis, the composition of respective materials can be analyzed simultaneously. Thus, the combinatorial analytical method is a great step forward, as there had been no definitive method for quick evaluation of multiple materials until now.

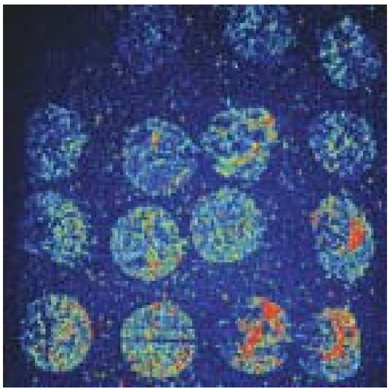


Fig. 1 X-ray fluorescence (XRF) image of combinatorial specimens (field of view: 8 mm x 8 mm). Red indicates areas with high Mn contents.

The **photo** in **Fig. 2** also shows a combinatorial specimen of a complex oxide of lithium and iron. Because this complex oxide chemically absorbs CO_2, it may play a key role in reducing greenhouse gases if its absorption capacity and rate can be increased. The specimen was synthesized under 4 different sets of conditions from the 1st to the 4th column, and was exposed to CO_2 under different conditions in each column. Using the synchrotron radiation from BL-16A1 at the Photon Factory, KEK, Tsukuba, Japan, X-ray absorption fine structure (XAFS) spectra of these materials were investigated by taking XRF images of the specimen while scanning incident X-ray energies. **Fig. 2** shows the XAFS of the 2nd material from the top. It was found that the absorption edge shifts to the high energy side in a short period of time, even under low-temperature exposure, indicating high CO_2 absorption power.

As can be seen in this example, by enabling simultaneous evaluation of multiple materials and selection of the material with the optimum properties, XRF imaging technique is a powerful tool for efficient development of high performance materials.

[This research was partially supported by SHISEIDO Grants for Scientific Research.]

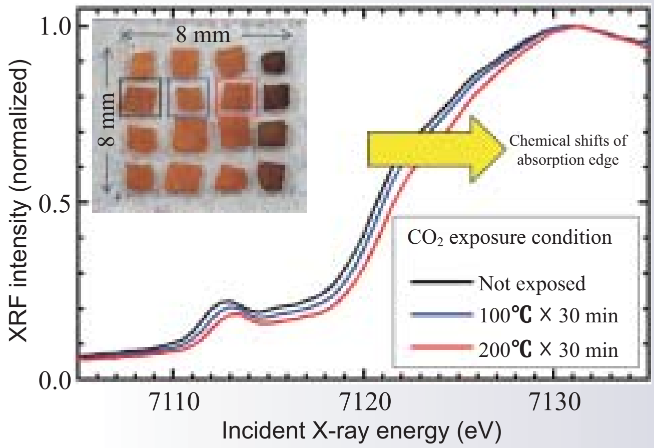


Fig. 2 Combinatorial specimen of Li-Fe oxide and fluorescence XAFS (Fe K absorption edge) of materials in squares. CO_2 absorption was confirmed by shift in absorption edge to the high energy side.

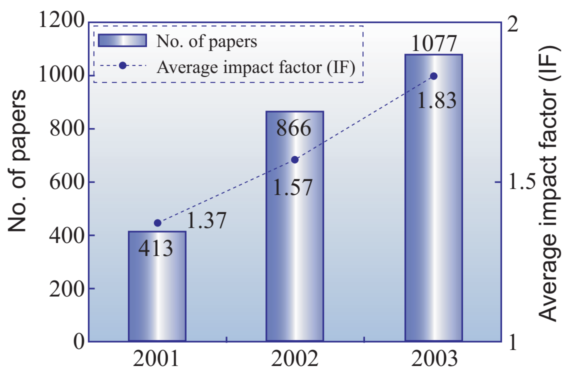
For further information, please visit: http://www.nims.go.jp/xray/lab/

NIMS Papers Show Strong Improvement in Both Numbers and Quality

In 2003, the number of original papers published by NIMS researchers in scientific journals surpassed the 1,000 mark for the first time and was approximately 2.6 times larger than in 2001. On average, this number was equivalent to about 2.5 papers/year by each regular researcher. The average impact factor (IF) of the journals where papers appeared has also increased by nearly 0.5 points in the last two years.

The IF statistic includes only papers published in journals which survey readers, ranging from 6 reports in the English journal *nature*, which has the highest impact factor to approximately 100 reports in Japanese journals and others with no IF.

Since its establishment as an independent research institute, NIMS has worked continuously to improve its research record. The results mentioned here are one result of these efforts.



NIMS NEWS

Full-Scale Kick-Off of International Center for Young Scientists (ICYS)

The International Center for Young Scientists (ICYS), as announced on the cover of our Vol.1 No.4 issue, is a program in which outstanding young scientists are employed as ICYS Research Fellows to carry out research in an independent and autonomous mode based on their own original ideas. The keywords of the ICYS Program are (1) youth-centered (2) internationalization, (3) interdisciplinary, and (4) independence and autonomy. The program uses English as a common language.

As a result of 3 candidate searches in 2003 (August, October, and December), NIMS received a total of 528 applications from 49 countries. Of these, 27 candidates from 16 countries were hired and have been arriving since October. As part of the program, we have assigned the ICYS Fellows to the same floors in the new Nano-Bio Building, creating an exciting environment where researchers from different fields and with different mentalities can work together in a spirit of friendly competition and mutual intellectual stimulation.

In principle, research by ICYS Fellows is conducted independently and autonomously. However, as a support system to ensure that Fellows can accomplish their research smoothly, NIMS has assigned more than 20 Scientific Advisers to the program. Fellows' research activities are also supported by administrative and technical staff with excellent English proficiency.

The ICYS Program, which was formally launched last September, will be based in the Nano-Bio Building completed in February. The move from temporary facilities to the new building has now been finished, and equipment for use by the ICYS, including an electron microscope, was delivered in March. In April, the program reached another important milestone, as 13 new Research Fellows took up their positions, marking the full-scale start of the project in fact as well as in name.

For details, please visit the ICYS homepage: http://www.nims.go.jp/icys/

NIMS NEWS

Completion of New Nano-Biomaterials Research Building

The new Nano-Biomaterials Research Building, which will serve as a base for nanotechnology research and biomaterials research at NIMS, was completed in February. Construction of the 5-story facility (height 30 m) began in October 2002. The building has total laboratory space of 4,928 m^2 and private research rooms of 1,958 m^2, and is equipped with clean rooms and a foundry for fabricating nano-bio devices. A research-related staff of approximately 200 will work in the building.

The 5^{th} floor and part of the 4^{th} floor will be used exclusively by international researchers in the ICYS program, and will have individual research rooms so that these outstanding young researchers from around the world can actively pursue original research.

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Publisher: Dr. Masatoshi NIHEI
Since: July, 2003

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