NIMS NOW

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Novel Laser Fabrication Techniques

—Laser Molecular Implantation and Polymerization Techniques for Organic Materials—

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Micro-nano Component Materials Group has successfully developed new techniques for injecting and fixing organic molecules in submicron arrays and shapes using laser implantation and polymerization, respectively.

Fabrication of micro-nano scale devices from organic materials requires site-selective implantation and fixing techniques for organic molecules in an extremely small size range and fixing/shape control techniques for organic materials. Lithography has long been used in the LSI industry as the main micro-nano fabrication technique for silicon materials, but it is a complex, multi-step process which requires large-scale equipment and a high level of operational technology. Moreover, unlike inorganic materials, organic materials tend to decompose when high energy beam injection and fabrication techniques are used.

To solve these problems, the authors independently developed a simple process technology that requires only focused irradiation with a laser light. This technology makes it possible to fabricate implantation arrays in an extremely small size range at the submicron order, or to perform fixing and shape control with multiple species of organic molecules, which will allow the user to select a diverse range of functions.

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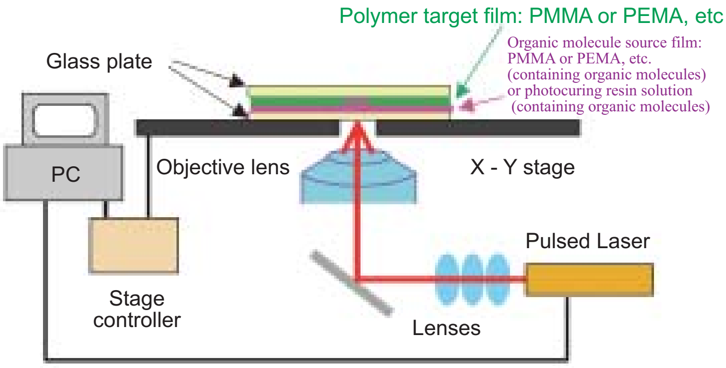

Fig. 1 Schematic diagram of laser molecular implantation (fixing) method.

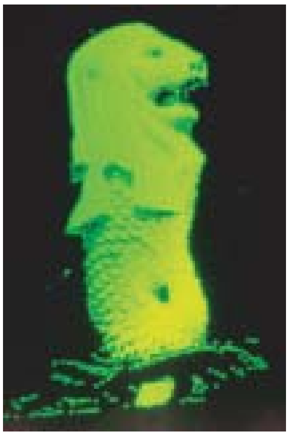

Fig. 2 Organic molecule (coumarin 6) implantation array pattern (width of lion image: approx. 400 μm).

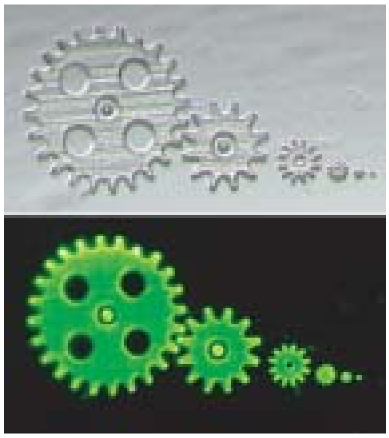

Fig. 3 Micro gears fabricated by laser polymerizaion technique (diameter: 160 μmΦ to 5 μmΦ).

Fig. 4 Fluorescence image of micro array of resin dots containing multiple species of organic molecules (340 μm x 530 μm).

In this issue

A Mild Immobilization Technique for Proteins

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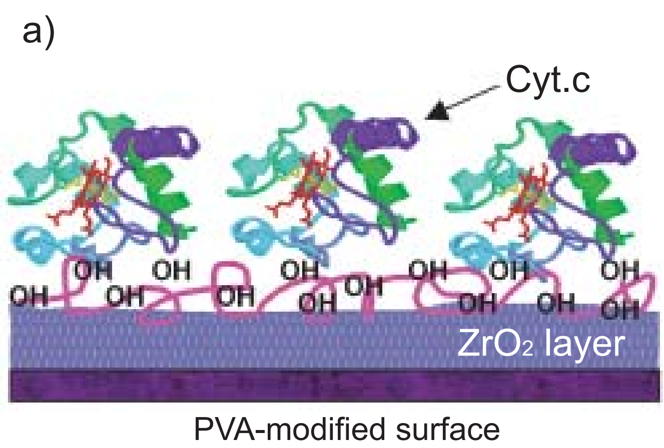
Remarkable progress has been achieved in technologies for fabricating organic thin films on the surfaces of solids in the last ten years. Today, ultrathin multilayer films of dye molecules, proteins, and macromolecules with thicknesses of several nanometers can be assembled in any arbitrary order, and organic thin films of these molecular substances can be fabricated even on the surfaces of minute particles and inner walls of micro- and nano-tubes. Furthermore, new functions of organic thin films can be realized by creating their composites with inorganic materials such as metals and semiconductors. From this viewpoint, organic thin films are identified as a strategic research field for NIMS.

The Macromolecular Function Oxides Group is engaged in research on new technologies which will enable us to immobilize proteins on the surface of inorganic materials while minimizing protein denaturation. The protein cytochrome c, which plays a key role in electron transfer in living organisms, is charged positively in neutral condition, and therefore is strongly adsorbed on the surface of negatively-charged metal oxides. However, because the folding structure is prone to collapse on the metal oxide surface, it is adsorbed as an insoluble denatured protein.

We discovered that this denaturation can be prevented by coating the surface of the metal oxide with an ultrathin organic layer, as shown in the conceptual diagram in **Fig. (a)**. Using a technique called "Surface Sol-Gel Process", a thin film of ZrO_2 with a thickness of 3.0-4.0 nm was deposited on a metal substrate, and a thin layer (1.6 nm) of polyvinyl alcohol (PVA) was then coated on this oxide film. Because the surface of the ZrO_2 is weakly charged negatively in neutral condition, it adsorbs cytochrome c. However, the uniform PVA layer prevents denaturation of the protein. We also found that proteins immobilized by this method completely desorbed in alkaline solution. The adsorption/desorption rate was constant during repeated experiment, as shown in **Fig. (b)**.

At present, we are pursuing research on the interaction between biomolecules and proteins on the surfaces of inorganic solids as a research strategy of organic thin films.



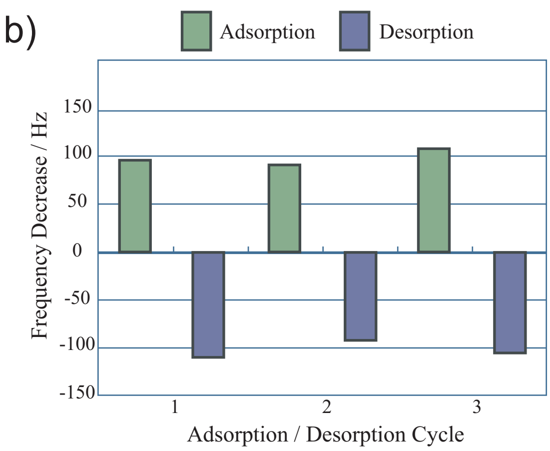


Fig. (a) Schematic illustration of cytochrome c on a metal surface modified with nanometer-thick ZrO_2 and PVA layers.
(b) QCM frequency changes during repeated adsorption and desorption of cytochrome c. The protein completely desorbs in alkaline solution.

Visit by the European Research Commission of the European Union

On December 5, 2003, NIMS was honored with a visit by members of the European Research Commission of the EU, including the Commissioner, H.E. Philippe Busquin. Talks focused on nanomaterials research and international cooperation between NIMS and its counterparts in the EU. The guests toured research facilities related to the research and development of nanomaterials such as SQUID (Superconducting Quantum Interference Device), nanotesters and atomic switches.

Visit by Director Hong and other Members of Korea's RIST

On November 7, 2003, Director Sang-Bok Hong of Korea's Research Institute for Industrial Science and Technology (RIST), Director Byoung-Hark Park of the Institute's New Materials and Components Research Center, and other RIST representatives visited NIMS for talks with President Kishi, Director Noda of the Materials Engineering Laboratory (MEL), Director Shintani, and others. This visit was one result of a Memorandum of Understanding on Research Cooperation concluded between RIST and MEL in July of last year.

RIST and MEL are currently involved in joint development of smart materials and devices utilizing those materials.

Molecular Device for Optically Controlled Single-Electron Tunneling

Yutaka Wakayama
Nanomaterials Assembly Group
Nanomaterials Laboratory (NML)

Application of single electron tunneling as a technology for power saving transistors and memory devices has been proposed, but before practical devices can be developed, it will be necessary to solve the problem of precise fabrication of nanoscale device structures with good reproducibility. From this viewpoint, organic molecules have several advantages as nanomaterials. For example, their size is extremely small, they have a uniform structure, and structural design using synthesis technologies is possible. The Nanomaterials Assembly Group therefore began development of devices which use the intermediate electrode in single electron tunneling.

Sample material was prepared by successively layering SiO_2, an organic molecule, SiO_2, and Au on an Si(100) substrate. In other words, the sample has a structure in which organic molecules are embedded in a metal-oxide-semiconductor (MOS) structure. Here, a porphyrin derivative molecule was used (**insert** in **Fig. 1**). The aim was to isolate the porphyrin molecules by placing high bulk substituents around the core skeleton. Measurement of the current/voltage characteristics of the sample material at cryogenic temperature (5 K) gave a step-like I-V curve, indicating that the porphyrin molecules function as an intermediate electrode, with single electron tunneling to this electrode (black line in **Fig. 1**). This device structure is similar to that of a single electron memory, demonstrating that single molecules can be used as a memory device.

High photo response is another advantage of organic molecules. Therefore, the same measurements were attempted with light irradiation. Under this condition, I-V characteristics change greatly, as shown by the blue line in **Fig. 1**. Furthermore, this change is reversible; when light irradiation is stopped, the I-V characteristics immediately return to their original state. This means that optical switching is possible with single electron tunneling (**Fig. 2**). This phenomenon is thought to involve a molecule excitation-relaxation process.

This result demonstrates that optical control of the input/output of a single electron in a single molecule is possible. This advantage of organic molecules is expected to contribute to the development of switching and memory in single electron devices and to new device applications which incorporate optical functions such as luminescence. This work was carried out as joint research with the Communications Research Laboratory (CRL).

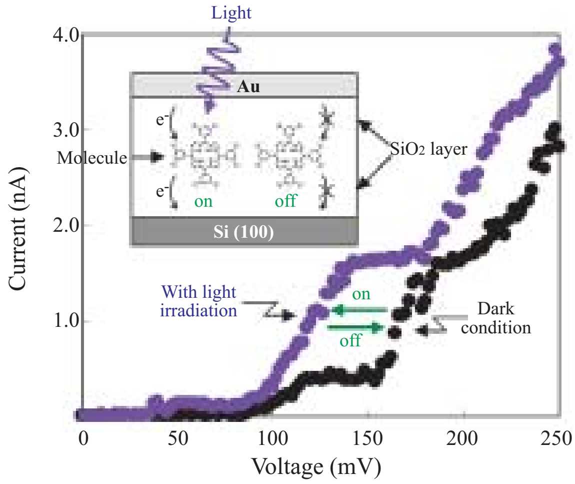


Fig. 1 Single electron tunneling phenomenon with organic molecule and its optical control.

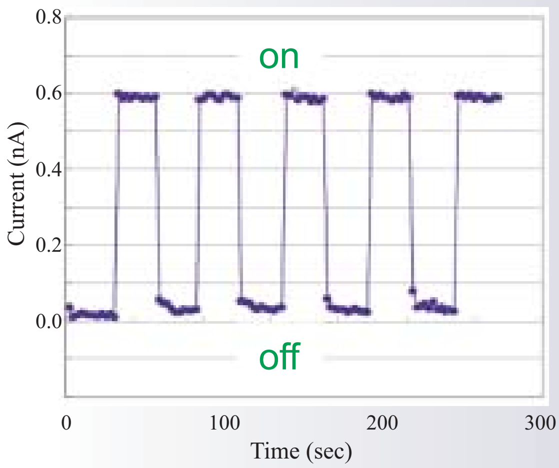


Fig. 2 Optical switching in single electron tunneling.

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Novel Laser Fabrication Techniques



Fig. 1 is a schematic illustration of the laser molecule implantation/fixing method. First, the functional organic molecule is dispersed in a polymer solution, which is spin-coated on a glass plate, creating a film that serves as the organic molecule source (source film). This plate and a second glass plate spin-coated with only a polymer film (target film) are placed together so that the two films are sandwiched between the plates. The organic molecules in the source film are then ejecting and implanting in a small region of the target polymer film by irradiating the source film with a focused laser beam. **Fig. 2** shows a micro dot pattern of pigment molecules (coumarin 6) fabricated by laser molecular implantation.

As a second technique, **Fig. 3** shows micro gears that were fabricated using a photocuring/photopolymerization resin solution containing added pigment molecules. Here, the laser was irradiated on the pigment-added solution, causing photocuring of resin limited to a specified shape. The remaining solution, which was not photocured, was then removed with ethanol. Using this technique, we also succeeded in fabricating a micro-shape of multiple kinds of molecules on a glass plate. (see **Fig. 4**).

These techniques, which provide simple processes for submicron level implantation and fixing of organic molecules, are expected to become important fabrication methods for nano-scale micro optical devices and nano-components for micro machines.

Research on Novel Phase-transition Phenomena in Organic Materials

—Insulator-Superconductor Transition in Magnetic Field—

Shinya Uji
Director
Nano Quantum Transport Group
Nano Materials Laboratory (NML)

With recent progress in organic synthesis technologies, it is now possible to synthesize organic materials (organic conductors) with a variety of structures and compositions. While these materials display high conductivity equal to that of ordinary metals, many organic conductors also exhibit interesting electrical and magnetic properties not seen in conventional metals and alloys. Researchers are therefore searching for means of applying these substances practically in novel materials which will take advantage of these properties. Moreover, because these properties are thought to originate in unique electronic states which exist in organic conductors, elucidation of the mechanism is also desired.

Noting that organic conductors have a large magnetic moment in crystals, the Nano Quantum Transport Group investigated their electrical and magnetic properties. Generally, superconductivity (zero electric resistance) becomes unstable with respect to energy and returns to the normal metal state (finite resistance) when a magnetic field is applied. However, with certain organic conductors, we discovered a phenomenon which is normally inconceivable, namely, an insulator-to-superconductor transition caused by the magnetic field.

This singular phenomenon was discovered in λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$, which is shown in the **insert** in the **accompanying figure**, with the composition x=0.45. The 2-dimensional BETS (bis(ethylenedithio)tetraselenafulvalene) organic molecular array and $FeCl_4$ molecular array have an alternating multilayer structure. Because the conduction electrons are located in the BETS molecule layers, this structure is characterized by a very easy flow of electricity in the BETS plane and resistance to electric flow in the direction perpendicular to this plane.

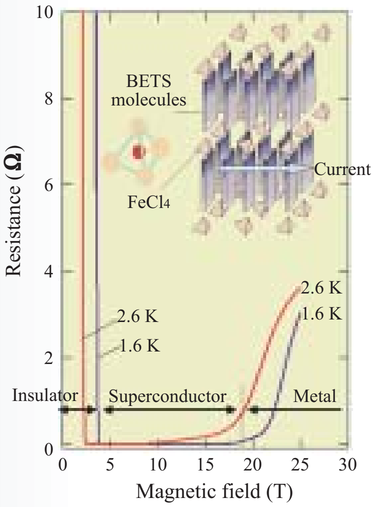

Fig. Magnetic field dependency of resistance of organic conductor λ-$(BETS)_2Fe_xGa_{1-x}Cl_4$ (x=0.45).
Insert: Schematic diagram showing crystallographic structure of λ-$(BETS)_2FeCl_4$.

As shown in the **figure**, at a cryogenic temperature of 1.6 K, resistance is extremely large in magnetic fields of less than 4 T, and the material is in an insulator state. However, we discovered that resistance abruptly drops to zero in a magnetic field of approximately 4 T. This striking phenomena is called an insulator-superconductor transition, and is triggered by the magnetic field. In higher magnetic fields, the superconducting state is broken and the material returns to a normal metal state. On the other hand, at higher temperatures, the range of the magnetic field where superconductivity appears becomes narrower, and at 5 K, superconductivity disappears completely.

This type of magnetic field-induced insulator-superconductor transition was first observed in the organic conductor mentioned above. At present, we are progressively gaining a more detailed understanding of the mechanism of this phenomenon. We believe that this mechanism will provide the basis for proposals on the development of materials which display stable superconductivity in extremely strong magnetic fields and new principles of operation for devices which enable precise control by an external magnetic field.

Visit by South Africa's Department of Science and Technology and Council for Scientific and Industrial Research (CSIR)

On January 22, representatives of South Africa's Department of Science and Technology and Council for Scientific and Industrial Research (CSIR), including Ms. Anati Judith Canca, General Manager of the Department of Science and Technology, visited NIMS for an exchange of views on future cooperation in research on high-temperature materials and environmental materials. During the visit, the South African officials toured the research facilities of the Electro-nanocharacterization Group (Nanomaterials Laboratory), High Temperature Materials Group (Materials Engineering Laboratory), and Photocatalysts Group (Ecomaterials Center). The Republic of South Africa is the 40th country to conclude a bilateral science and technology cooperation agreement with Japan.

3-Day Forum for Exchange of Ideas with Directors

In December, NIMS held a 3-day exchange of ideas on research to encourage interdisciplinary fusion and strength cooperation between researchers and research groups. Directors and others presented their views on respective approaches to research and the outlook for the future, followed by a vigorous exchange of opinions. This event was held December 22-25, 2003.

New Phthalocyanine-type Near-infrared Absorbing Dyes

Hiroaki Isago
Materials Physics Group
Materials Engineering Laboratory (MEL)

Phthalocyanines (abbreviated as Pc) are used in numerous practical applications and are the object of applied research in a wide range of fields, including IT, medicine, energy, and the environment (**Fig. 1**). These compounds also meet many of the requirements placed on functional organic materials. Considering this potential, this class of substances is considered one of the most promising of all chemical compounds.

To take advantage of the wide-ranging functions of Pc compounds, the Materials Physics Group succeeded in synthesizing complexes of antimony (Sb) and bismuth (Bi) for the first time, which had not been accomplished by any previous researcher. In clarifying the properties of these new Pc complex compounds, in particular, we found that the Pc complexes containing Sb show unique properties which run counter to the common sense about conventional Pc pigments. As one example, the optical absorption spectra of Pc complexes containing trivalent Sb (**Fig. 2A**) and pentavalent Sb (**Fig. 2B**) are shown in Fig. 3. Unlike the known Pc pigment (C), which absorbs visible light (red), the absorption maximum wavelength of these new Pc compounds is in the near-infrared (NIR) region. In addition to application to infrared cut filters for plasma displays and CCD, development of materials with absorption bands close to the output wavelength of semiconductor lasers (780, 830, 870 nm) is expected to open the way to a wide range of applications, including optical disks, photodynamic therapy of cancer, electronic photography, electronic printing, and dyes for currency counterfeiting prevention.

Our near-term goal is to control the absorption wavelength and improve the solubility and stability of these Pc dyes by various modifications of the groups, X and R in **Fig. 2**. In the case of dye A, we are also trying further shift of the absorption band to longer wavelength and amplification of the band intensity by utilizing molecular aggregation phenomena, because this type of dye can be applied to nonlinear optical materials.

In addition to practical synthesis of these compounds, we also hope to gain a theoretical understanding of the mechanism of absorption in the NIR region through research in collaboration with universities and others as the basis for constructing a new synthetic strategy.

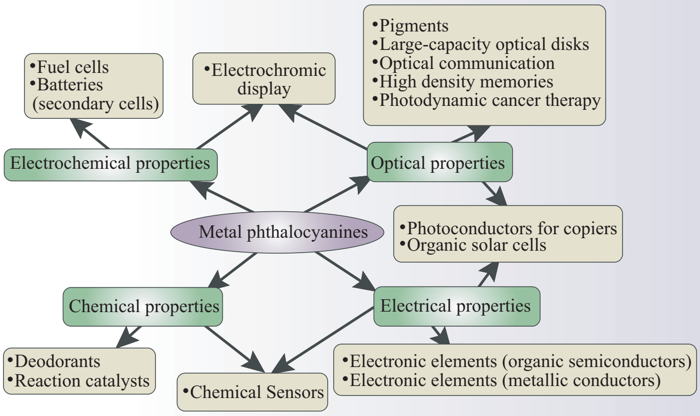

Fig. 1 Functions and applications of phthalocyanine.

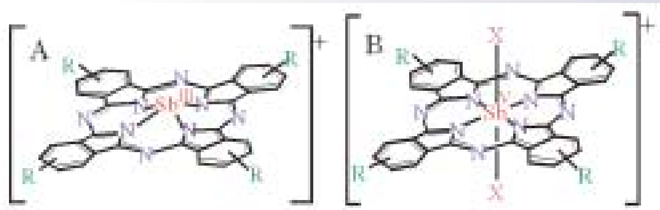

Fig. 2 Novel NIR dyes synthesized in the present research.
(Pc complexes containing (A): trivalent Sb and (B): pentavalent Sb)

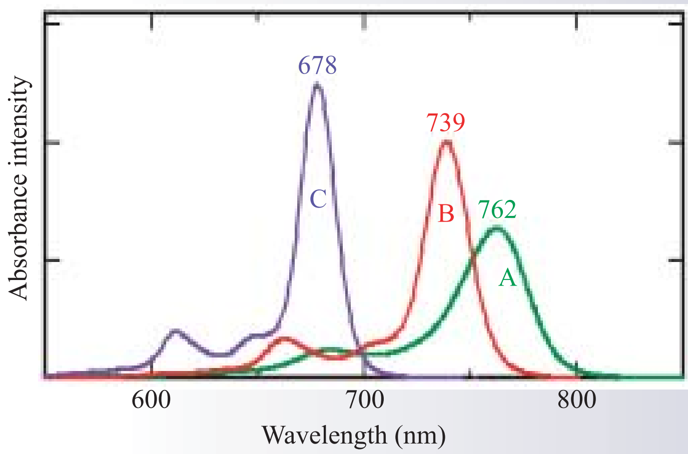

Fig. 3 Optical absorption spectra of the new NIR dyes.
A: trivalent Sb complex, B: pentavalent Sb complex, C: known Pc dye.

Observation of Interference Phenomena in Silicon Crystals in Femtosecond Region

A NIMS group including researcher Muneaki Hase and Director Masahiro Kitajima of the Materials Engineering Laboratory (MEL), working jointly with a group headed by Prof. Hrvoje Petek of the University of Pittsburg in the United States, has succeeded for the first time in observing interference phenomena in silicon in the femtosecond (10-15 second) ultra-high speed time region. These results give a direct view of the origins of how electrons act on the crystal lattice and how the lattice imparts force to electrons, providing new insight into the emerging research field of quantum dynamics, which takes as its object ultra-high speed interaction between particles. This work is also expected to help establish basic principles for the development and evaluation of nanoelectronic devices. These results were published in the Nov. 16 edition of the English science journal *Nature*.

Nerve Regeneration Material using Biodegradable Polymer

Atsushi Matsuda
Hisatoshi Kobayashi
Artificial Organ Materials Group
Biomaterials Center (BMC)

—Development of Chitosan Tube Derived from Crab Tendon—

When nerve tissue is damaged as a result of labor or traffic accidents, operations to remove malignant tumors, or similar trauma, the patient may suffer loss of perceptual and sensory functions and paralysis of motor functions, greatly reducing quality of life (QOL). At present, the principal therapeutic methods proposed for nerve damage are (1) transplantation of the patient's own tissue and (2) nerve tissue regeneration methods using artificial tubes.

With method (1), it is necessary to take nerve tissue from a healthy area, which can cause aftereffects (sequela). In contrast, aftereffects are not a concern with method (2), because injured peripheral nerves are connected using an artificial tube, and the nerve tissue regenerates in the inside of the tube. However, for this type of treatment, it is necessary to develop tubes with bioaffinity, biodegradability, and high strength.

The Artificial Organ Materials Group, in cooperation with Tokyo Medical and Dental University (Associate Prof. Soichiro Itoh, Prof. Kenichi Shinomiya) developed a tube for use in nerve tissue regeneration using crab tendons as the material.

Crab tendons have a high bioaffinity and are made up of biodegradable chitin and calcium phosphate, which is the main component in teeth and bones. They also contain a small amount of protein and fat, etc. Because chitin molecules have a molecularly arrangement, they possess high mechanical strength.

First, the unnecessary calcium phosphate and protein are removed by chemically treating the crab tendon. A tube is then fabricated by alkali treatment of the chitin component to produce chitosan. To accelerate regeneration of the nerve tissue, we are also studying on a modification of the laminin peptide, which is a cell adhesive molecule, to the chitosan tube by covalent bonding (see **Fig. 1**).

Fig. 2 shows a chitosan tube which was produced from a crab tendon. This tube was actually transplanted to the sciatic nerve of a rabbit. The micrographs of the nerve tissue in **Fig. 3** were taken 8 weeks after transplantation, and show that the nerve tissue with the tube transplant has regenerated to the same degree as the nerve tissue transplanted from the animal itself, while keeping the shape of the chitosan tube.

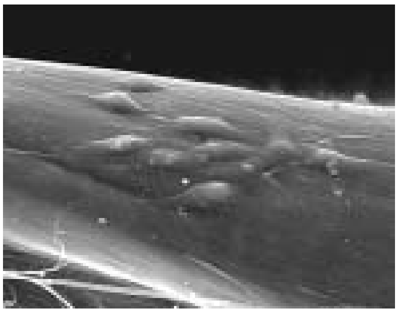

Fig. 1 Regenerating nerve cells observed as protuberances on chitosan tube fabricated from crab tendon (direction of nerve protuberances is aligned with orientation of chitosan).

Future goals include more rapid regeneration of nerve tissue using a nerve cell nutritional factor.

Fig. 2 Chitosan tube for use in nerve regeneration.

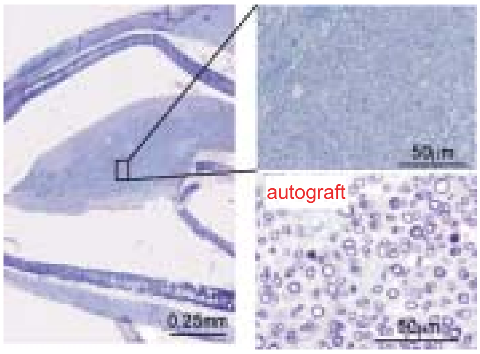

Fig. 3 Regenerated tissue when chitosan tube was transplanted to sciatic nerve of rabbit (left and upper right: transplantation of chitosan tube; lower right, transplantation of rabbit's own nerve tissue).

Atomic-resolution Characterization of Silicon Surface in Ultra-low Temperature Region

A group led by Senior Researcher Daisuke Fujita of the Nanomaterials Laboratory (NML) has succeeded for the first time in atomic-resolution characterization of the ultra-low temperature ground state of atoms on a silicon surface in a cryogenic environment at below 1 K. In an ultra-high vacuum, ultra-low temperature environment at 0.7 K (approximately -272 ℃), it was possible to identify the stable structure in the two types of periodic structures which exist on the surface of silicon with a (100) crystal plane. This is considered an extremely important discovery, as it provides indispensable basic knowledge for precision process and simulation technologies. This research was carried with funding by the Japanese government's Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Start of Joint Development of Inexpensive, Non-allergic Dental Devices

Director Takao Hanawa and Researcher Daisuke Kuroda of the Reconstitution Materials Group, Biomaterials Center (BMC), and an R&D team of Dentsply-Sankin k.k. have started a joint project for development of dental devices using a nickel-free stainless steel with high mechanical strength and corrosion resistance. The aim of this joint project is to develop an economical manufacturing technology for dental devices, which are small and complex in shape, through a fusion of Dentsply-Sankin's advanced dental device manufacturing technologies and the new NIMS Ni-free stainless steel. This new manufacturing technology for dental devices will enhance mechanical strength, corrosion resistance, and biocompatibility. This project group plans to put Ni-free stainless steel dental devices on a market during fiscal 2004.

Biomedical application of Polymer Gel as Tissue Adhesive

Tetsushi Taguchi
Artificial Organ Materials Group
Biomaterials Center (BMC)

—Crosslinking of Biomacromolecules with Citric Acid Derivative—

Polymer gels can be obtained by crosslinking of organic molecules. For example, biomacromolecules gels prepared using crosslinkers are used as tissue adhesives with high bonding strength. Existing clinical adhesives employ aldehyde compounds as crosslinkers, but this class of substances has high cytotoxicity and the presence of residual crosslinkers can delay wound healing. The development of a low toxicity crosslinker would solve this clinical problem.

The Artificial Organ Materials Group first decided to synthesize crosslinkers. Our attention was drawn to citric acid, as it is found in living organisms. This suggested that a new crosslinker synthesized using citric acid could be metabolized in the patient's body, solving the problem of residual crosslinkers. We therefore synthesized a new citric acid derivative (CAD) as a crosslinker by modifying the carboxyl groups in citric acid with electron-attracting groups (succinimidyl groups). We also developed a new binary-type adhesive consisting of the newly-synthesized crosslinker and organic macromolecules (**Fig. 1**).

Initially, we investigated the bonding strength of the developed adhesive using the skin of a live mouse. **Fig. 2** shows the tearing strength of two pieces of skin joined with the adhesive. Skin joined with the adhesive developed in this work showed extremely high strength, equal to that of the conventional aldehyde-type adhesive. In previous research, we demonstrated that high adhesive strength can be obtained using porcine soft tissue. However, this substance does not contain living cell components. The present experiment has shown that high bonding strength can also be obtained under conditions approximating clinical use.

Therefore, the next issue is toxicity with respect to living organisms. To examine this point, the adhesives were introduced under the skin of mice, and the tissue reaction was investigated after 7 days. As shown in **Fig. 3**, the aldehyde-based adhesive caused an extremely strong inflammation reaction, whereas virtually no inflammation was observed with the newly developed adhesive. The new adhesive decomposed and was absorbed, and the tissue has almost completely recovered its normal condition.

The use of medical adhesives to close wounds after surgical operations eliminates the need for post-operative suture removal, reducing the time required for surgical procedures while also lessening the physical and mental burden on the patient and reducing post-operative management.

Animal experiments with this adhesive are now being conducted jointly with the Institute for Clinical Medicine of University of Tsukuba, and research aimed at clinical application is in progress.

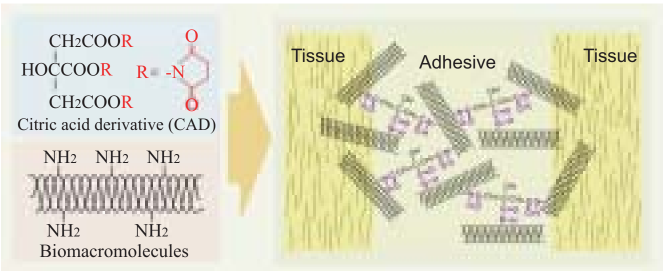

Fig. 1 Reaction of adhesive at tissue-tissue interface.

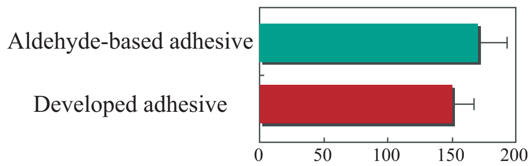

Fig. 2 Bonding strength of developed adhesive in experiment with mouse skin (g / cm²).

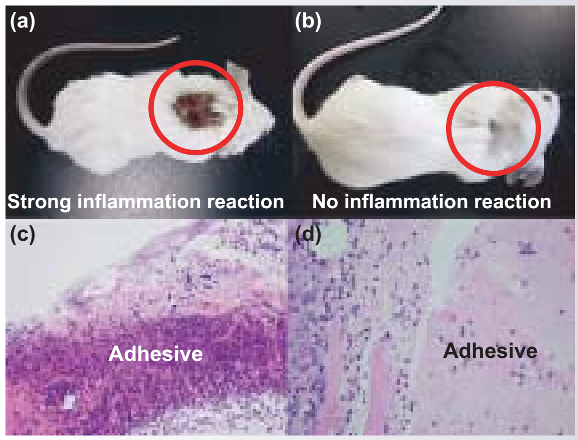

Fig. 3 Tissue reaction after introduction of adhesives under mouse skin (condition after 7 days).
(a, c: aldehyde-based adhesive, b, d: developed adhesive)

Successful Introduction of Internet Electron Microscope in the Science Classroom

A group including Director Kazuo Furuya and other members of the NIMS Nano-characterization Group, Nanomaterials Laboratory (NML), in cooperation with Super Science High schools (SSH) designated by Japan's Ministry of Education, Culture, Science, Technology and Sports (MEXT), has successfully introduced the internet electron microscope in high schools, enabling remote operation, observation, and analysis via the internet. A connection test of the system was carried out previously with the National Museum of Emerging Science and Innovation (MeSci: Odaiba/Tokyo), and a considerable volume of data was acquired through test operation. The start of operation in the actual educational situation with the two designated SSH schools will have an important impact on science and technology education as a whole, and is also expected to be extremely useful in science education and research-related fields.

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