Chapter 5

Summaries

5.1 Thin film fabrication and site-selective deposition

Site-selective deposition (SSD) of thin films has been realized and micropatterns of them have been fabricated in our study. We have reported direct SSD of amorphous TiO_2 thin films (in chapter 2.3, 2.4, 2.5). A patterned SAM of OTS which has silanol groups and octadecyl groups was used as a template. Amorphous TiO_2 were selectively deposited on silanol regions using , the hydrolysis reaction of precursors such as titanium dichloride diethoxide or tantalum ethoxide from solutions or vapor and produced micropatterns of thin films that had high feature edge acuity.

Moreover, site-selective immersion was realized using a SAM having a pattern of hydrophilic and hydrophobic surfaces (in chapter 3.4) (Fig. 1 (b)). In the experiment the solution containing Ti precursor contacted the hydrophilic surface, and briefly came in contact with the hydrophobic surface. The hydrophilic surface solution was replaced with fresh solution by continuous movement of bubbles, thus anatase TiO_2 was deposited and thin film was grown on the hydrophilic surface selectively. This technique can be used to fabricate any kind of micropattern so long as the film can be deposited from a solution.

SSD of thin films was realized using a seed layer (in chapter 3.3) (Fig. 1 (c)). We used a quartz crystal microbalance (QCM) to evaluate in detail the process by which anatase TiO_2 is deposited from an aqueous solution and found that nucleation and initial growth of it were accelerated on amorphous TiO_2 thin films compared with on octadecyl, phenyl, amino or hydroxyl (silanol) groups. In this process amorphous TiO_2 was shown to decrease the nucleation energy of anatase TiO_2 and provided nucleation sites for the formation of anatase TiO_2. Amorphous TiO_2 thin film was deposited on silanol regions of patterned OTS-SAM from TDD solution. This substrate was immersed in an aqueous solution containing Ti precursor to be used as a template for SSD. Anatase TiO_2 was selectively deposited on amorphous TiO_2 regions to form thin films and thus a micropattern of anatase TiO_2 thin films was successfully fabricated.

Pattern of anatase TiO_2 thin films was fabricated in an aqueous solution at 50 °C (in chapter 3.5) (Fig. 1 (d)). The patterned SAM having OTS regions and silanol regions was immersed in a solution containing a Ti precursor and subjected to ultrasonication for several hours. The difference in adhesion strength of thin films on substrates was employed for the site-selective elimination method. Heterogeneously nucleated TiO_2 and homogeneously nucleated TiO_2 particles adhering to the OTS-SAM could be easily eliminated from the substrate by ultrasonication, whereas those on silanol groups maintained their adhesion during the immersion period. TiO_2 can form chemical bonds such as Ti-O-Si with silanol groups, but cannot form them with octadecyl groups, resulting in the difference in adhesion strength, which is the essence of the site-selectivity of this method. The site-selective elimination method can be applied to fabricate nano/micro-scaled patterns in the solution by the immersion of the substrate that has regions on which depositions adhere strongly and regions on which depositions adhere weakly, enabling elimination by treatment such as ultrasonication.

Mechanisms and site-selectivities for SSD were proposed as shown above. These site-selectivites were proposed by the use of scientific knowledges obtained by the investigations of interactions and chemical reactions between functional groups of SAMs and ions, clusters and homogeneously nucleated particles in the solutions. Our investigations and proposals would contribute to the development of the field of site-selective depositions to fabricate future nano/micro devices in environmentally friendly conditions. This study also showed the ability of nature-guided processing for fabrication of nano/micro devices.

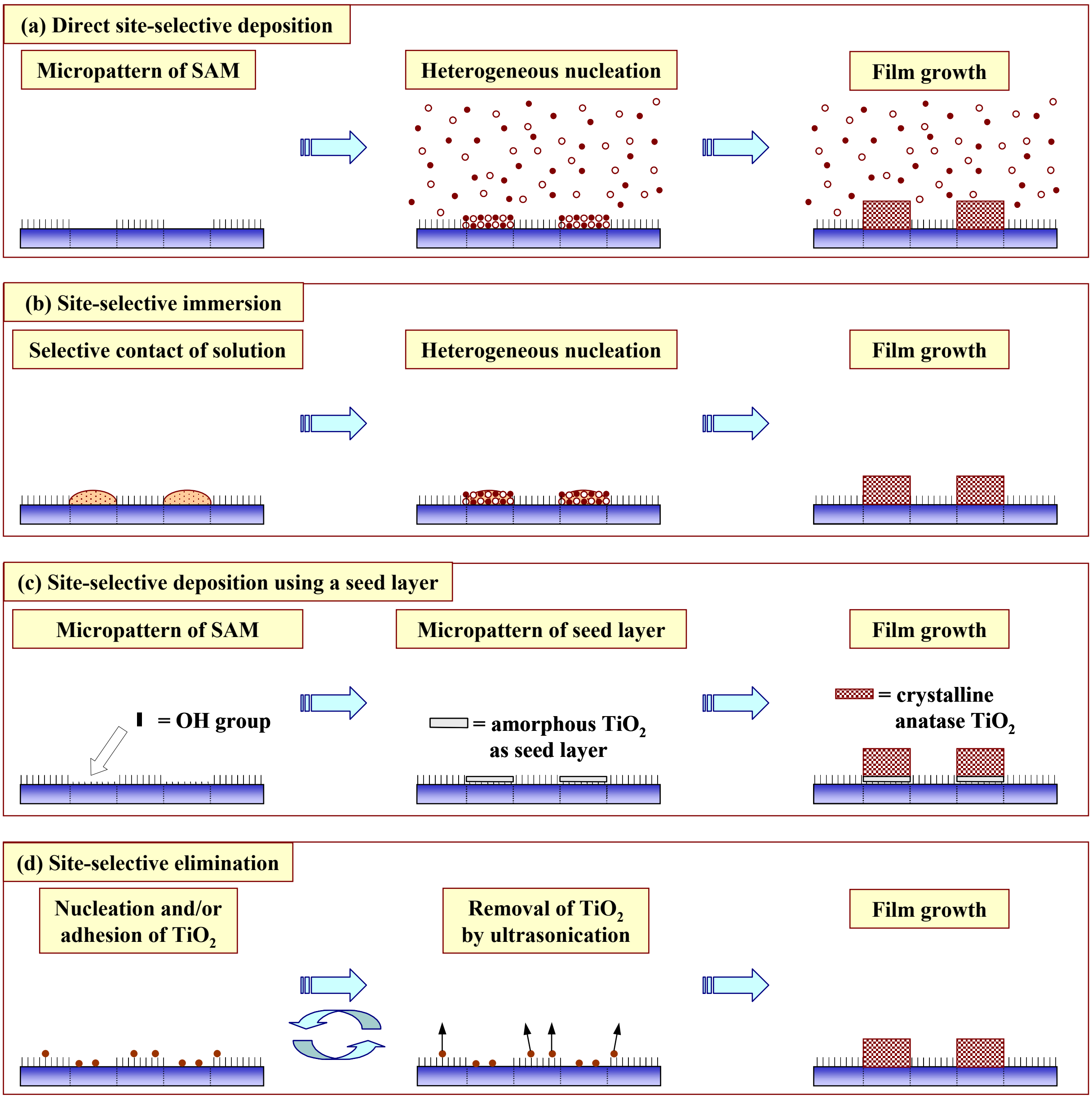

Figure 1. Conceptual processes for site-selective deposition of thin films by (a) direct site-selective deposition, (b) site-selective immersion, (c) site-selective deposition using a seed layer or (d) site-selective elimination.

5.2 Particle assembly and patterning

Interactions between nano/micro particles and functional groups of SAMs were investivsted to realize particle assembly and patterning of particles. Several self-assembly processes were propsed to fabricate fine structures constructed from particles in environmentaly friendly conditions.

Patterns of nano/micro particles were fabricated in the solution using interaction between particles and SAMs. Patterned SAMs were used as template to deposit particles on desired positions. Micropatterns of randomly deposited particles were fabricated using electrostatic interaction (in chapter 4.5) (Fig. 2 (a)) or formation of chemical bonds (in chapter 4.3, 4.4) (Fig. 2 (b, c)) first. Two-dimensional ordinaly particle arrays were then fabricated in solution through the formation of siloxane (Si-O-Si) or ester bonds (-COO-) at room temperature (in chapter 4.5) (Fig. 2 (b, c)). Selective immobilization of single particles into predetermined positions with respect to adjacent particles was further realized by nanolithography using an AFM probe (in chapter 4.5) (Fig. 2 (c)). Additionally, patterns of close-packed particle monolayer and several kinds of particle wires were fabricated using electrostatic interaction (Fig. 2 (a)) or the formation of chemical bonds (Fig. 2 (b, c)) (in chapter 4.5).

Molecular recognition, chemical bond formation and/or electrostatic interaction can be used for site-selective deposition in the solution. Additionally, self-assembly fabrication can be realized by the solution process. Solution processes have many advantages compared with other processes such as manipulation technique or mechanical arramgement thechique, and the advantages of solution process allowed us to fabricate nano/micro particle structures self-assembly in environmentally friendly conditions.

Furthermore, drying process of colloidal solution was studied and novel patterning methods were proposed to realize precise arrangement of particles. Two-dimensional self-assembly of spherical particles was fabricated using a liquid mold and its drying process (in chapter 4.6) (Fig. 2 (d)). We fabricated particle wires that have high accuracy of arrangement at room temperature on hydrophilic regions of a patterned SAM. Particles were assembled to have regularity in their array by capillary force in the drying process. Assembly of particles was obtained in hydrophilic regions that were covered with solution containing particles and was not obtained in hydrophobic regions that were not covered with solution. Liquid mold determined the positions for particle assembly resulting in high site-selectivity for patterning compared with the patterning in the solution. Additionally, a self-assembly process to fabricate separated particle wires was proposed, and particle wires constructed from a close-packed multi-particle layer or mono-particle layer were realized on OTS-SAM from ethanol solution (in chapter 4.7) (Fig. 2 (d)). A substrate was immersed into the solution containing particles perpendicular to the liquid surface and the liquid surface was moved downward by evaporation of solution. Particles formed a mono/multi-particle layer and the particle layer was cut by the periodic drop-off of the solution. This process allowed us to fabricate the orderly array of particle wires and to show the high ability of the self-assembly process for fabrication of nano/micro-structures constructed from nano/micro particles.

Particles were assembled to have regularity in their array by capillary force in the drying process. Patterns of a close-packed particle layer and particle wires were fabricated in the solution previously (Fig. 2 (a, b, c)) (in chapter 4.2, 4.3, 4.4). However, severe control of many factors was necessary to realize a close-packed structure and high accuracy because capillary force cannot be used in the solution. A close-packed structure can be easily obtained in drying process compared with the process in the solution. The capillary force is one of the advantage of the drying process, although solution process have an advantage that various molecular recognitions can be used in the soliution.

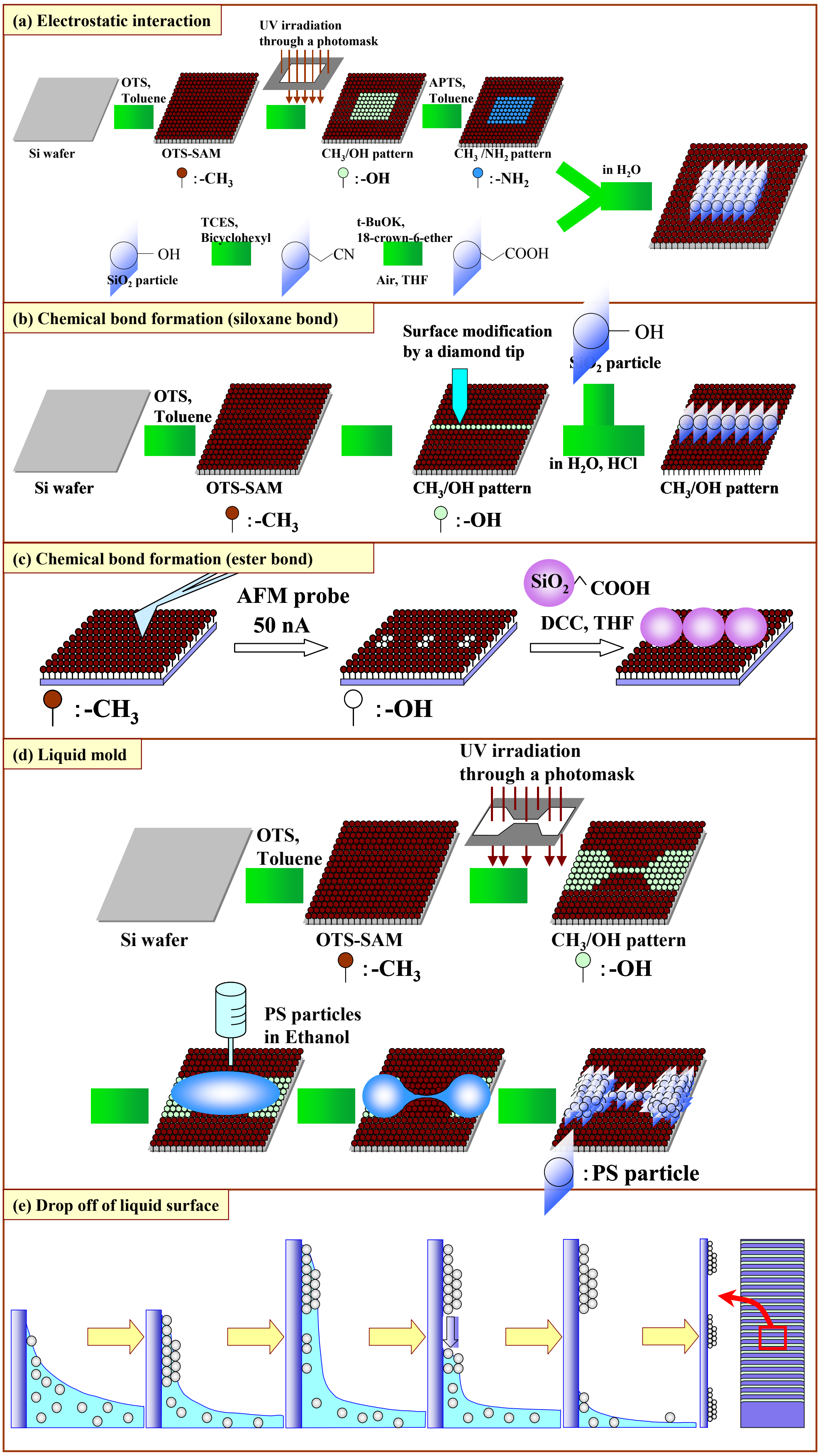

Figure 2 (a-f). Conceptual processes for site-selective deposition of nano/micro particles.

5.3 Surface modification and patterning of SAM

We also developed surface modification of SAMs to be applied for site-selective deposition of thin films and particles. We realized nano/micropatterns of SAMs by UV irradiation (Fig. 1, 2 (a, d)), mechanical modification (Fig. 2 (b)) or electrical modification using AFM probe (Fig. 2 (c)).

Novel surfacemodification of SAMs and patterning methods were proposed to fabricate nano/microstructures constructed from thin films or nano/micro particles, and the basic mechanisms of them were discussed. These novel methods would contribute to the development of site-selective deposition and self-assembly integration of nano/micro units such as particles to be applied for future devices.

5.4 Discussions of my study in the field of research

We have investigated interactions and chemical reactions between organic materials and inorganic materials, especially on functional groups of SAMs. Furthermore, novel methods were proposed for site-selective depositions of inorganic thin films and nano/micro particles in the solutions with the use of knowledge of our study, and realized them in environmentally friendly conditions. The field of site-selective deposition of inorganic thin films and nano/micro particles using SAMs in the solutions was established by this study.

Chapter 6

General conclusions and Future prospects

6.1 General conclusions

We have proposed novel mechanisms and site-selectivities for SSD. These site-selectivites were proposed by the use of scientific knowledges obtained through the investigations of interactions and chemical reactions between functional groups of SAMs and ions, clusters and homogeneously nucleated particles in the solutions. The field of SSD of inorganic thin films and nano/micro particles using SAMs in the solutions was established by our study. And our investigations and proposals would contribute to the development of the field of site-selective depositions to fabricate future nano/micro devices in environmentally friendly conditions. Furthermore, the study showed the ability of nature-guided processings for fabrications of nano/micro devices. It was shown that we can learn many things from nature for the production of materials and devices. Nature-guided processing and science will hopefully be developed in wake of our study and will hopefully provide a solution to serious global problems.

6.2 Future prospects

We have proposed novel methods to fabricate nano/micropatterns of thin films and nano/microstructures from particles, and realized nano/micropatterns of them in an environmentally friendly condition. However, our goal is to develop environmentally friendly methods to fabricate nano/micro-sized functional devices such as nano/micro-patterns of functional thin films or particles with a minimum amount of energy consumption and mass. Concretely speasking, we have been trying to fabricate nano/micropatterns of thin films from a harmless substance, in the desired position (without using the etching process and thus avoiding wastes), with a one-step process from raw material to device (or to material having the desired composition and shape) without preparation of substances, at ordinary temperatures and atmospheric pressure, in an environmentally friendly condition such as an aqueous solution. We have been also trying to fabricate nano/microstructures from particles by self-assembly using the same concepts as for the patterning of thin films. Considering this eventual goal, we have not crossed the finish line yet.

Moreover, various properties are required to apply the nano/micro structures of thin films or particles for the devices. Further improvement of regularity, ordinality and feature edge acuity of nano/micro structures constructed from thin films or particles is necessary to apply them for optical devices such as photonic crystals. Additionally, novel structures such as diamond structure which show effective photonic band gap should be prepared with the patterning and self-assembling techniques. Particle assemblies also need to be fixed using chemical bonds between particles or plastic coating to apply them for optical mobile devices. On the other hand, not only feature edge acuity of patterns but also chemical composition and crystal structure of the films should be improved to apply patterns of thin films for electronic devices such as the gate oxide layer in MOSFET. Amorphous TiO_2 thin film prepared by our method showed some properties (k = 25~ 30 (>30 nm thick), ρ= $1.22\times10^{12}\Omega$cm (at 1V), L.C. 1.3×10^{-7}A/cm^2 (at 1V), B.F. >6.0MV/cm (at 10V)) (ref. 4 in page 129), however, further improvement of the various properties such as frequency response characteristic and stability of amorphous phase though the control of OH values in the films, chemical composition, uniformity, grain size, grain boundary, degree of crystallinity, and so on are strongly reqired. In other words, the improvement of required properties as devices as well as the improvement of patterning method is needed to apply them for devices. Further advance is required to apply our environmentally friendly method for future devices.

List of Achievement

1. Papers

1.1 Thin film fabrications and their site-selective depositions

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11. Yoshitake Masuda, Shinichi Wakamatsu, and Kunihito Koumoto, "Site-selective Deposition and Micropatterning of Tantalum Oxide Thin Films Using a Self-assembled Monolayer", *J. Euro. Ceram. Soc.*, in press.

12. Yoshitake Masuda, Noriko Saito, Rudolf Hoffmann, Mark R. De Guire, Kunihito Koumoto, "Nano/micro-patterning of anatase TiO_2 thin film from an aqueous solution by site-selective elimination method", *Sci. Tech. Adv. Mater.*, in press.

1.2 Particle assembly and their patterning

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3. Reviews

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4. Patents

1. "Micropatterning of TiO_2 Thin Films using Self-assembled Monolayers and Titaniun Alkoxide"
   Japanese Patent Application Number: 2000-282927
   Inventor: Mitsuhide Shimohigoshi, Kunihito Koumoto, Yoshitake Masuda
   Applicant: TOTO Ltd.
   Filling Date: Sep. 18, 2001
2. "Photonic Crystals and Their Production Methods"
   Japanese Patent Application Number: 2001-151248
   Inventor: Kunihito Koumoto, Yoshitake Masuda, Akio Harada, Takashi Okawa
   Applicant: Daiken Chemical Co., Ltd.
   Filling Date: May 15, 2002
3. "Site-selective Immersion Method"
   Japanese Patent Application Number: 2002-137641
   Inventor: Yoshitake Masuda, Kunihito Koumoto
   Applicant: Nagoya Industrial Science Research Institute
   Filling Date: May. 13, 2002
4. "Patterning of Metal Particles and Production Method of Ceramic Electronic Components"
   Japanese Patent Application Number: 2002-227796
   Inventor: Kunihito Koumoto, Yoshitake Masuda, Akio Harada
   Applicant: Kunihito Koumoto, Daiken Chemical Co., Ltd.

Filling Date: Aug. 5, 2002

5. "Fabrication of Metal Thin Films and Production Method of Ceramic Electronic Components"
   Japanese Patent Application Number: 2002-363249
   Inventor: Kunihito Koumoto, Yoshitake Masuda, Peixin Zhu, Ryosuke Ueyama, Akio Harada
   Applicant: Kunihito Koumoto, Daiken Chemical Co., Ltd.
   Filling Date: Dec. 16, 2002
6. "Novel fabrication method for patterning of particle assembly"
   Japanese Patent Application Number: 2003 – 148094
   Inventor: Yoshitake Masuda, Kunihito Koumoto
   Applicant: Nagoya Industrial Science Research Institute
   Filling Date: May 26, 2003
7. "Surface midification of polymer using silicon solution"
   Japanese Patent Application Number: 2003 – 150799
   Inventor: Peixin Zhu, Yoshitake Masuda, Makoto Teranishi, Osamu Takai, Kunihito Koumoto
   Applicant: Nagoya Industrial Science Research Institute
   Filling Date: May 28, 2003
8. "Novel fabrication methods of tantarium oxide thin films"
   Japanese Patent Application Number: 2003 - 172803
   Inventor: Yoshitake Masuda, Kunihito Koumoto
   Applicant: Nagoya Industrial Science Research Institute
   Filling Date: June 18, 2003
9. "A novel fabrication method of dielectric thin films"
   Japanese Patent Application Number: 2003 - 174214
   Inventor: Yanfeng Gao, Yoshitake Masuda, Kunihito Koumoto
   Applicant: Nagoya Industrial Science Research Institute
   Filling Date: June 19, 2003

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