Chapter 1

Introduction

1.1 Background

By opting for a life of convenience, humans consume large amounts of mass (substance, raw materials) and energy. In particular, the amount of energy consumed by humans in just the past 100 years is extraordinary in relation to the long history of humankind and Earth. Such large-scale consumption is causing serious environmental changes.

Green & Sustainable Chemistry

From this perspective, concepts for chemistry to save our planet such as "Green Chemistry (formal nomenclature in U.S.A[1], U. K., Italy, common name in Japan)", "Green & Sustainable Chemistry (GSC ; formal nomenclature in Japan)", "Sustainable Chemistry (in Germany)", "Environmentally Benign Chemistry", "Environmentally Friendly Chemistry", "Clean Chemistry" were proposed.

Green & Sustainable Chemistry in U.S.A.

The U.S. government announced the proposal of "The Presidential Green Chemistry Challenge" in 1995[1]. P. Anastas *et al.*[2] in EPA (Environmental Protection Agency in U.S.A.) stated "Green chemistry is the use of chemistry for pollution prevention. More specifically, green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. Green chemistry is a highly effective approach to pollution prevention because it applies innovative scientific solutions to real-world environmental situations."[1] and showed 12 Principles (in appendix)[2] of Green Chemistry. Additionally, "The presidential Green Chemistry Award" and "Green Chemistry and Engineering Conference" were started in 1995, 1997, respectively.

Green & Sustainable Chemistry in Japan

The meaning of "Green & Sustainable Chemistry" defined by Japanese Green Chemistry Workshop[3-4] in 1999 is "GSC is the chemical engineering to realize "Health and safety of human and environment" and "Resource saving and energy saving" by the technical innovation considering all life cycle of products such as product design, raw material selection, production method, usage, recycle and so on.". Green Chemistry Study Group was established by

Chemical Society of Japan in 1999 and Green Sustainable Chemistry Network was established in 2000[3].

Green & Sustainable Chemistry in Europe

On the other hand, these fileds have also been developed in Europe[3]. International conference, "The Green Chemistry : Challenging Perspective" was held in Italy (1997). GCN (Green Chemistry Network) was established by RSC (Royal Society of Chemistry in U.K.) in 1998[5]. The conference about Sustainable Chemistry was held in Germany (1999)[6]. Institute for Prospective Technological Studies in Joint Research Center (EU) researched Sustainable Technologies from 1998 and issued the report "Innovation and cleaner technologies as a key to sustainable development : the case of the chemical industry" in 2000. "Woehler Preis, Ressourceschonends Prozesse (Germany)", "Awards for Clean Chemical Products and Processes (Italy)", "UK Green Chemistry Awards (U.K.)" were established in 1998, 1999, 2000, respectively.

Materials science in Green & Sustainable Chemistry

"Green & Sustainable Chemistry" includes all materials, products, processes, recycles, environmental consequence, resources, and so on. The concept of "Green & Sustainable Chemistry" includes those of "Soft chemistry" ("Chimie douce" in French), "Biomimetic materials chemistry", "Bioinspired materials chemistry", "Soft-solution processing", and so on. Importance of "Green & Sustainable Chemistry" has been grown rapidly and materials science should also contribute to the development of "Green & Sustainable Chemistry".

In the field of materials science, material having the desired composition and shape should be fabricated by the use of minimum raw materials (substance) and energy. The fabrication processes and the products should be environmentally friendly for hundreds-of-years. In the case of eletro- or optical-devices of thin films, nano/micropatterns of thin films should be fabricated 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. From this perspective, we tried to develop the fabrication processes for nano/micro devices such as patterns of thin films or particles with the concept of "Green & Sustainable Chemistry".

Appendix

12 Principles[2] of Green Chemistry showed by P. Anastas *et al.* in EPA.

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

1.2 Thin film fabrications and their patterning

1.2.1 Thin film fabrications in the solutions

Background : Concepts of sustainable environmental chemistry for thin film fabrication

Humans have consumed large amounts of mass (substance, raw materials) and energy. However, the concepts to develop environmentally friendly processes have been proposed from last of 20 century.

"Soft chemistry" ("Chimie douce" in French)[1-2] was proposed in Frace in 1970s. Soft solution aims for the realization of "materials processing under moderate conditions".

"Biomimetic materials chemistry" and **"bioinspired materials chemistry"** were introduced by S. Mann[3]. Many inorganic materials such as amorphous silica (opal phytolith, plant opal); iron oxides (magnetite, etc.); calcium carbonates (aragonite, calcite, etc.); calcium phosphates (hydroxyapatite, etc.); and alkaline-earth surfates ($SrSO_4$, etc.) were prepared in aqueous solution systems learn from nature.

"Soft-solution processing"[4-6] refers to low-energy fabrication methods that use aqueous solutions to create shaped, sized, located, and oriented materials – a concept extended from "soft solution" which emphasizes low-energy routes to the synthesis of chemical compositions and crystal structures. These concepts articulate a vision for materials science and materials processing in the 21st century.

Background : Solution processes of sustainable environmental chemistry for thin film fabrication

Furthermore, several solution processes have been developed under the influence of these concepts.

Sol-gel process[7-8] is the solution process in which solid phases are formed through gelation of a colloidal suspension.

Electrodeposition allows us to deposit pure metals, alloys, semiconductors, ceramics, and polymers on a variety of substrates. For instance, highly crystallized ceramic thin films, such as $BaTiO_3$, $SrTiO_3$, $LiNiO_2$, $LiCoO_2$, $PbTiO_3$, and $LiNbO_3$ can be electrodeposited on metallic substrates from aqueous solutions at low temperatures (25-200 °C)[9-11].

Hydrothermal reaction can be defined as any heterogeneous chemical reaction in the presence of an aqueous solvent above ambient temperature and at a pressure greater than 1 atm in a closed system[12]. Crystalline thin films such as $BaTiO_3$, $SrTiO_3$, $LiNbO_3$, and $LiCoO_2$ can be grown on various substrates with this method.

Furthermore, the main techniques for non-electrochemical synthesis of polycrystalline ceramic films from aqueous solutions at low temperatures, and some of the materials produced using them, are as follows:[13-16]

Chemical bath deposition (CBD)—CoO^{16}, $Co_3O_4^{17}$, NiO^{18-20}, AgO^{21}, Ag_2O^{21}, ZnO^{22-27}, $CdO^{22,\,28-29}$, $In_2O_3^{30}$, SnO_2^{31}, $Cd_2SnO_4^{23}$; CdS, ZnS, Sn_xS, PbS, MnS, CoS, NiS, Cu_xS, Ag_2S, As_2S_3, Sb_2S_3, Bi_2S_3, MoS_2, and corresponding selenides (see reviews in Refs. (32-35)).

Successive ion layer adsorption and reaction (SILAR)—$MnO_2^{36)}$, $FeOOH/Fe_2O_3^{37)}$, $NiO^{38)}$, Cu_2O^{39-40}, CuO^{41}, ZnO^{42-49} and ZnO with Ni, Cu, or Cd doping[50], $Tl_2O_3^{51}$, SnO_2^{52}, $LaNbO_x^{53}$, CeO_{2+x}^{54} and Y, La and Eu hydroperoxide[55]; ZnS^{56-57}, $CdS^{56,\,58-59}$, PbS^{60}, CoS^{61}, CuS^{62-63}, Ag_2S^{64}, $Sb_2S_3^{65-66}$, $In_2S_3^{67}$ and $Bi_2Se_3^{68}$.

Electroless deposition (ED) with catalyst (Ag^+, Sn^{2+}, or Pd^{2+})—MnO_2^{69}, $La_{1-x}MnO_3^{70}$, ZnO^{71-72}, $In_2O_3^{73}$, $Tl_2O_3^{69}$, $\alpha\text{-}PbO_2^{74}$.

Liquid phase deposition (LPD)—SiO_2 (see reviews in Refs. (75)), TiO_2^{76-82}, ZrO_2^{83}, $V_2O_5^{84-85}$, $\beta\text{-}FeOOH/\alpha\text{-}Fe_2O_3^{86}$, $NiFe_2O_4^{78}$, $LnMO_3$ (Ln = La, Nd; M = Cr, Mn, Fe, $Co)^{87-88}$, SnO_2^{89}. Liquid-phase deposition is an aqueous technique for deposition of oxide films that has been widely used for SiO_2^{90-91} but is being increasingly studied as a route for films of oxides such as $TiO_2^{76-77,\,92-97}$ and others.[14]

Purpose and novelty of our study --- TiO₂ thin films

Hydrolysis reaction of titanium compound

We have tried to develop a solution process to from uniform amorphous TiO_2 thin film and realize site-selective deposition of them. Sol-gel technique can form amorphous film in the solution, however, many particles and clusters formed in the solution deposit on a whole area of substrates such as patterned SAMs. Thin films should be formed without sol (many particles and clusters) to realize site-selective deposition. We thus tried develop the solution process in

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which titanium compounds are hydrolyzed to form solid thin films directly without the formation of sol. Additionally, we tried to hydrolyze titanium compounds only on desired area by the use of a patterned SAM. Titanium conpounds can form chemical bonds with silanol groups and they are hydrolyzed to form films by adsorbed water molecules on silanol groups of a patterned SAM. We proposed a novel solution process which can ralize site-selective deposition of amorphous TiO_2 thin films, and we tried to show the ability of site-selective depsotion and develop the field of site-selective deposition.

Liquid phase deposition of anatase TiO_2

Liquid phase deposition of anatse TiO_2 was developed by S. Deki. This excellent process provides crystalline anatase TiO_2 in an aqueous solution at low temperature. This slution process has high value and high impact to show high ability of site-selective deposition, we thought. We focused on the development of site-selective deposition processes, not the development of a solution reaction itself. We tried to develop many valuable site-selective deposition processes to show high ability of "site-selective deposition". We tried to develop the field of site-selective deposition by the proposals and experimental proofs of site-selective deposition of anatase TiO_2 thin films.

1.2.2 Titanium dioxide thin film

Background : Amorphous TiO$_2$

The silicon-based microelectronics industry is rapidly approaching a point where device fabrication can no longer be simply scaled to propressively smaller sizes[1-2]. The continual increase in device density as the minimum feature size of the lithography is reduced. Device densities for both DRAM and Inorganic devices (for example, CMOS FETs) are shown in Fig. 1[1]. The continued aggressive scaling of VLSI gate oxide according t Moore's Law begins to face barriers by entering into a tunneling regime that results in the inability to scale the oxide further. The gate oxide layer has very small thickness as shown in a schematic cross-section of a field effect transistor (FET) (Fig. 2)[1]. According to the International Technology Roadmap for Semiconductors (ITRS), loe-power devices will require an equivalent oxide thickness (EOT) of ≤ 15 Å for the 65 nm technology node[2], while high-performance devices require an EOT of ≤ 10 Å. For low power consumption applications where the gate leakage current requirement is below 10^{-7} A/cm^2, a high-k dielectic thin film – one which is thermally stable and chemically stable in contrast with silicon – is needed.

The major issue and fundamental limitation for further scaling of the gate dielectric is the tunneling current's exponential increase due to the reduction in thickness. When the thickness is reduced to the direct quantum mechanical tunneling regime, gate leakage current increases exponentially. Gate dielectrics with higher dielectric constants must be formed in order to reduce leakage current while maintaining the same gate capacitance. Also, a material with a large band gap and barrier height is needed.

Because of these requirements, simple metal oxide films such as ZrO$_2$[3], HfO$_2$[4], Al$_2$O$_3$[5], Y$_2$O$_3$, Ta$_2$O$_5$[6-7], TiO$_2$[8], and ferroelectric barium strontium titanate (BST) films have been suggested forgate dielectrics, though the number of candidates will be reduced by the study in this field.
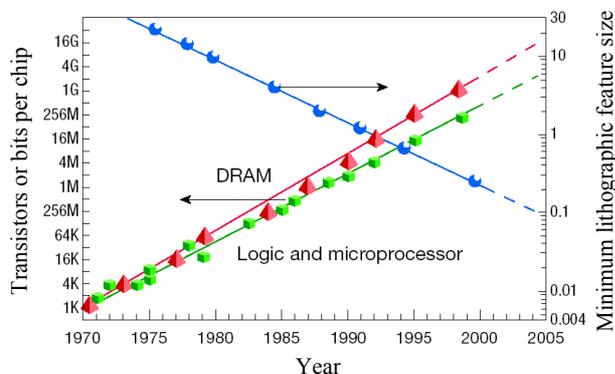

Fig. 1 Device densities for both DRAM and Inorganic devices (for example, CMOS FETs).
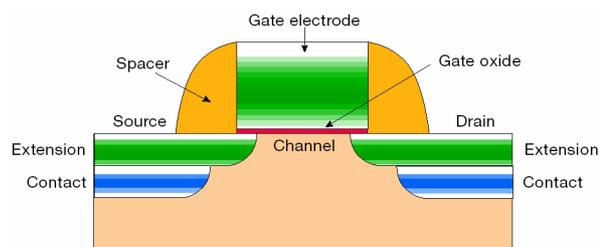
Fig. 2 Schematic cross-section of a field effect transistor (FET).

These thin films have been prepared with physical processes such as MBE (molecular beam epitaxy) or MOCVD (metalorganic chemical vapor deposition) using special device, high vacuume and/or high temperature.

We focused on amorphous TiO_2 because of its wide applications including gate oxide in MOS-FET, halmlessness, bountiful resources compared with other candidates for gate oxides. TiO_2 has been given great attention enough to demonstrate and show the high ability of environmentally friendly processes such as bio-inspired chemistry, green chemistry or soft solution process. Additionally, required properties for gate oxide in MOS-FET are very high and these high requirements are worthy enough to be our target to show the ability of environmentally friendly processes.

Background : Anatase TiO₂

Anatase TiO_2 has many attractive properties such as high refractive index, high dielectric constant, photocatalysis, super hydrophilisity and so on. TiO_2 thin films are thus of interest for use in various applications including microelectronics[6], optical cells[10], solar energy conversion[11], highly efficient catalysts[12], microorganism photolysis[13], antifogging and self-cleaning coatings[14], gratings[15], gate oxides in MOSFETs (Metal-Oxide-Semiconductor Field Effect Transistor)[16-17], photonic crystals and so on. Accordingly, fabrication of thin films and nano/micro-patterns of TiO_2 has been attempted by several methods. Crystallie TiO_2 is one of the representative oxides and attracts the attention in ceramic field, and thus crystalline TiO_2 is suitable for the target of our study to show high ability of aqueous solution processes.

We focused on amorphous TiO_2 and anatase TiO_2 because these oxides have many attractive properties and applications such as gate oxide in MOS-FET (amourphous), photonic crystal (anatase) or photocatalysis (anatase), and because TiO_2 and titanium are harmless substances existing a lot in nature. The nano/micro patterns of TiO_2 thin films should be most appropriate to show high ability of environmentally friendly processes such as bio-inspired chemistry, green chemistry or soft solution process.

Background : thin film fabrication and patterning of TiO₂

TiO_2 films were prepared from solutions via various methods[18-34] and micropatterning of TiO_2 was attempted by a number of methods[35-37] referring to these thin film fabrication processes. A micropattern of anatase TiO_2 thin films was fabricated on a patterned self-assembled monolayer (SAM) by lift-off process[22]. Phenyltrichlorosilane (PTCS)-SAM

was irradiated by ultraviolet light through a photomask to form a silanol/phenyl micropattern to be used as a template. Anatase TiO_2 thin films were deposited on the entire area of a patterned SAM from $(NH_4)_2TiF_6$ aqueous solution with the addition of H_3BO_3 at 50 °C for 6 h. The TiO_2 thin film deposited on a substrate was a solid timber and the film was dried in air to form numerous cracks for the subsequent lift-off process. Thin films on phenyl regions were then peeled off along the cracks by sonication. Thin films on the silanol region showed strong adhesion to silanol groups compared to those on the phenyl regions. Consequently, a micropattern of anatase TiO_2 was fabricated at low temperature. However, the lift-off process caused a deterioration of feature edge acuity of the micropattern. A novel process to realize site-selective deposition is required for fabricating a micropattern with high feature edge acuity.

Lin *et al.*[32] synthesized TiO_2 gel films on the SAM of octadecyltrichlorosilane (OTS) using $Ti(OC_3H^i_7)_4$-derived TiO_2 sols. OTS-SAM induced precipitation of anatase phase at rather low temperature of 200 °C and accelerated anatase-to-rutile phase transformation when a mole ratio of $H_2O : Ti(OC_3H^i_7)_4$ as low as 0.5 was employed for sol preparation. TiO_2 thin films were also deposited in aqueous HCl solutions of $TiCl_4$ on SAMs with SO_3H groups[33]. The films consisted of TiO_2 crystallites around 120 nm in size. Desu[34] reported a method for preparing TiO_2 films at 170 - 240 °C by exposing silicon substrates alternatively to $TiCl_4$ and H_2O vapors under vacuum. In his model for the film formation mechanism, $TiCl_4$ initially reacts with silanol groups on the silicon surface.

Patterned TiO_2 thin films were deposited from 0.5M $TiCl_4$ aqueous solution on 6M HCl at 80 °C for 2 h[35-36]. Regions of the SAM containing sulfonate surface functionality were produced via photo-oxidation (UV light 254 nm) of initially deposited thioacetate groups through a mask. During aqueous deposition of TiO_2 onto such engineered substrates, nanocrystalline anatase TiO_2 particles deposited on the sulfonate groups of the monolayer. TiO_2 particles were selectively deposited, with a micropattern formed at low temperature. But thin film consisted of particles nucleated and grown in the solution, thus lowered film uniformity. Tremel and colleagues[37] described the TiO_2 micropattern. Gold-coated glass slides have been patterned by stamping using hexadecane thiol SAMs. Using thiol terminated with a styrene monomer, micropatterns (polystyrene/hexadecane) were formed on the surface by graft polymerization of styrene. These patterned gold slides were then used as a template for TiO_2 precipitation from ethanolic solutions of $Ti[OCH(CH_3)_2]$ (titanium isopropoxide) with additional water vapor. TiO_2 was precipitated throughout the template after immersing at room temperature for 10 h. Following polymer cleavage, TiO_2 over polystyrene was removed, and a patterned TiO_2 having feature edge acuity better than 1 μm was thereby obtained. Unfortunately, the deposited TiO_2 film displayed many cracks and TiO_2 particles. Improvement of feature

edge acuity is mandatory if these patterns are applied to electrical or optical devices.

Purpose and novelty of this study

We proposed novel concept and processes for site-selective deposition of thin films in environmentally friendly conditions and tried to show high ability of environmentally friendly processes such as bio-inspired chemistry, green chemistry or soft solution process. Candidate for gate oxide in MOS-FET which requires high properties was tried to be fabricated in the solution process. This will show the abitilty of solution process and that physical process such as silicon technogoly can import the concept from chemical processes. Additionally, nano/micro patterns of crystalline anatase TiO_2 was tried to fabricate from an aqueous solution. We tried to show the high ability of aqueous solutions to prepare ceramic devices. Ceramic devices would be shown to fabricate through environmentally friendly conditions such as aqueous solutions without high temperature treatment.

Summary of results and framework of this paper

We proposed processes to prepare amorphous TiO_2 thin films from the solution (in chepter 2.3) or the gas phase (in chepter 2.5) and realized site selective deposition on patterned SAMs. Uniform amorphous TiO_2 thin films were fabricated with our method and site-selective deposition of uniform amorphous TiO2 was realized using molecular recognition on patterned SAMs for the first time. Mechanisms of depositions were further discussed in chapter 2.4 (solution process) and 2.5 (gas phase process).

Several site-selective depsotion processes were proposed in chapter 3.3, 3.4, 3.5 and patterns of crystalline anatase TiO_2 thin films were fabricated from an aqueous solution. These processes can be applied to site-selective deposition of other thin films deposited from solutions. These processes extended the field of site-selective deposition. Deposition mechanism and crystal orientation were further discussed in chapter 3.6. Science of thin film deposition would be progressed and deposition of crystalline thin films from aqueous solutions will be controlled with this discussion .

1.3 Particle assembly and patterning

Background : Particle assembly and patterning

Particles show various interesting properties[1] that are not observed in the bulk form of a material. Recently, monodispersed particles have been synthesized by various methods. Particles may be thus treated as if they were atoms, and one-, two- or three-dimensional arrangement of particles have been studied by many researchers. For instance, photonic crystals can be constructed by monodispersed particles. Additionally, electronic energy transfer in close-packed CdSe[2] or InP[3] quantum dots arises from dipole-dipole inter-dot interactions between proximal dots. For instance, the metal-insulator transition was observed in a silver quantum dot monolayer.[4-5] In order to apply these novel properties for future devices, precise particle arrangement techniques must be developed.

Assembly techniques of fine particles have been studied by several groups[6-14] (Table 1). Assembly of Au particles was realized by a casting method[8-9] at first. The electrostatic interaction was also used for assembly and alternate adsorption of Au particles.[11-12] Yonezawa *et al.*[14] demonstrated that the close-packed ammonium layer of an adsorbed bi-layer provides superior binding sites for negatively charged Au particles (19 nmφ). They are mostly adsorbed in a closely packed arrangement, due to the regular, dense disposition of positive charges on the surfaces. This research confirmed that alternate layer-by-layer assembly is possible in this system. Furthermore, a closely packed layer of polystyrene particles (1 μmφ) was fabricated using the capillary attractive force, and the optical properties of this particle array was studied.[14] Particles are successfully assembled in an orderly arrangement in this array. Xia e*t al.*[15] brilliantly fabricated large colloidal crystals with their (100) planes of fcc structure oriented parallel to the substrate, which has a two-dimensional regular array of square pyramidal pits. 3D opaline lattices having such orientation over areas as large as several square centimeters were constructed from polystyrene particle (250 nmφ, 480 nmφ, 1.0 μmφ) in the solution through self-assembly. This technique does not need special devices such as electron beam writing in the assembling process and the silicon templates should be robust enough to be used many times.

Patterning of assembled particles was realized by several methods[16-36] (Table 1). Micropatterns of randomly deposited particles were fabricated by gas jet[16-17], ink jet[18-19] printing methods or electrostatic interaction.[20] J. Aizenberg *et al.*[20] supported substrates micropatterned with anionic and cationic regions in a particle suspension for 2 min. The substrates were then removed and rinsed the excess suspension. The observation of drying process of this wetted substrate showed the particles within each negatively charged regions moved towards the center of the circles and formed dense clusters. They fabricated micropatterns of randomly deposited particles and dots using electrostatic interactions and a drying process. Whitesides *et*

Table 1 Assembling and patterning techniques of particles.

Assembling methods	Particle	Structue	Reference
casting	Au, Pt, Ag (1~10nm ϕ)	two-dimensional hexagonal structure	8)
casting	Ag	ring of Ag particles	9)
alternate adsorption (macromolecule)	Au	monolayer, multilayer	11)
alternate adsorption (amphiphilic molecule)	Au (20 nm ϕ)	monolayer, multilayer	12)
laser standing-wave field (laser trap)	Polystyrene(1μm ϕ), TiO$_2$(0.24μm ϕ)	two-dimensional close-packed structure	13)
capillary force	Polystyrene(1μm ϕ)	two-dimensional close-packed structure	14)
flow cell using array of pits	Polystyrene(250nm ϕ, 480nm ϕ, 1μm ϕ)	(100)-oriented colloid crystal	15)
Patterning methods			
Gas jet depositioning	various kinds of particles (nm~μm ϕ)	micropattern of randomly deposited particles	16-17)
Ink jet printing	ZrO$_2$ (100-200 nm ϕ)	micropattern of randomly deposited particles	18-19)
Electrostatic and lateral cappilary interaction	Polystyrene(1μm ϕ)	micropattern of randomly deposited particles, dot	20)
Electrostatic interaction	Au (10μm ϕ)	micropattern of randomly deposited particles	21)
Electrostatic interaction	SiO$_2$ (710nm ϕ), Latex (530-1000nm ϕ)	micropattern of randomly deposited particles	22)
Chemical bonds	Zeolite (1.6×1.2×0.6μm)	micropattern of randomly deposited particles	23)
Probe manipulation	Au (50-100μm ϕ)	two- and three-dimensional structure, particle tower	24-25)
Electrophotography method	SiO$_2$ (5μm ϕ)	micropattern of randomly deposited particles, dot	26-28)
Micro mold method	Al$_2$O$_3$ (47μm ϕ)	dot, particle tower etc.	29)
Probe manipulation.	Latex (0.6-2μm ϕ)	micropattern of close-packed structure, fcc structure	30-31)
Micro mold method	polymer (450 nm ϕ)	micropattern of close-packed structure	32)
Photolithography and etching	Si (855nm ϕ)	micropattern of close-packed structure etc.	33-34)
AFM lithography	Latex (190-1000nm ϕ)	dot	35)
Patterns of grooves	SiO$_2$ (840nm ϕ)	micropattern of colloid crystal	36)

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al.[21] used electrostatic interactions to direct the patterning of gold disks having 10 μmφ on functionalized surfaces. The micropattern of gold disks was successfully fabricated by environmentally friendly processes such as the solution process at room temperature. This technique does not need special devices and conditions, and can be applied to not only planer substrate but also curved substrate such as a fiber. Hammond *et al.*[22] fabricated micropatterns of SiO$_2$ particles (710 nmφ) or latex particles (530 nmφ, 1 μmφ) on a patterned polyelectrolyte multilayer in solution at room temperature using electrostatic interactions. They demonstrated control over the density and selectivity of particle adsorption using a polyelectrolyte multilayer platform and adjustment of three conditions: pH of the colloid suspension, ionic strength of the suspension and concentration of added surfactant. Yoon *et al.*[23] modified the surface of zeolite and a glass substrate with several functional groups. Micropatterns of zeolite were fabricated on the glass substrates in solution by various covalent linkages. These techniques extended the variety of patterning methods and introduced strong adhesion in particle assembly.

Two-dimensional patterns with regular repeatability in the particle array were also made by some techniques such as probe technique[24-25], electrophotography method[26-28] and micro mold method.[29] In addition, patterns with high arrangement accuracy have been realized by some techniques. Miyazaki *et al.* [30-31] fabricated photonic crystals such as two-dimensional closely packed structure[30] and fcc (or hcp) structure[27] from Latex particles (0.6 ~ 2 μmφ) by the micro-manipulation technique in a scanning electron microscope. Though this can be applied to many kinds of particles and it is possible to arrange particles to an accuracy of several percent, this technique requires hours for the arrangement. Kim *et al.*[32] fabricated micropatterns of fcc (or hcp) structure from polymer particles (200 nmφ) using a micro mold. The mold was adhered to silicon substrate, and the particle suspension was then poured into clearance between the mold and the substrate. After drying, the mold was removed and microstructures were obtained. However, the position of individual particles can't be controlled and a highly precise mold is required for the arrangement of nano-sized particles. Patterning of close-packed three dimensional structure (fcc) constructed from silicon particles was also fabricated using photolithography and etching techniques. Planar, single-crystalline silicon photonic crystals that have low defect densities can be obtained by assembling a thin layer of colloidal particles on silicon substrate.[33-34] Mirkin *et al.*[35] arranged polystyrene latex particles (190 nmφ, 930 nmφ, 1 μmφ) on MHA (16-mercaptohexadecanoic acid) dots deposited by holding the AFM probe. The technique can realize precise arrangement of nano/micro particles. Ozin *et al.*[36] described two processes, microfluidic colloid crystal self-assembly and spin-coating colloid crystal self-assembly, for particle assembly on silicon wafers. Patterns of

V-shaped grooves inside a Si (100) were prepared by chemical etching to be used as templates for microfluidic assembly. A drop of an aqueous dispersion of SiO_2 particles (840 nmφ) was added at the interface between the patterned silicon wafer and the flat block to fabricate the patterns of fcc colloid crystal parallel lines. Additionally, a particle suspension was spread on the wafer having an array of square pyramid-shaped etch pits by spin coating. (100)-oriented colloid crystals having fcc structure were formed in etched pits within 2 h. Colloid crystals were fabricated rapidly within lithographic patterned silicon grooves by these self-assembly processes under moderate conditions.

Purpose and novelty of our study

In this study, we have tried to develop self-assembly processes to fabricate nano/micro patterns of particles in environmentally friendly condition using molecular recognitions, chemical reactions and electrostatic interactions. We tried to show high ability of self-assembly process for nano/micro patterning of particles. Concretely speaking, we have tried to fabricate nano/micropatterns of particles in the desired position (without using the etching process and thus avoiding wastes), with a self-ssembly process, in an environmentally friendly condition such as an aqueous solution, with a harmless substance, without preparation of substances, at ordinary temperatures and atmospheric pressure. We have been trying to develop self-assembly processes of nano/micro particles. We utilized molecular recognitions, chemical reactions and electrostatic interaction in the solution (chapter 4.3, 4.4, 4.5) and capillaly force in drying processes (chapter 4.6, 4.7).

Summary of results and framework of this paper

Patterns of randomly deposited particles were fabricated in the solutions using chemical reactions (in chapter 4.3, 4.4). Patterns of close-packed particle layer and particle wires were fabricated on patterned SAMs using several interactions (in chapter 4.5). Surface modification of SAMs was also discussed in chapter 4.5. Furthermore, drying process of solution was utilized for particle assembly. Patterns of close-packed or non-close-packed particle layer were fabricated using drying process of liquid molds (in chapter 4.6). Array of particle wires was fabricated without a patterned template using drying process in chapter 4.7. These prosesses showed high ability of self-assembly process for fabrication of particle structure.

1.4 References

---1.1 Background---

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(2) Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.

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---1.2 Thin film fabrications and their patterning---

---1.2.1 Thin film fabrications in the solutions---

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