

**Patterning of TiO₂ Thin Films and Particles
using Self-assembled Monolayers**

Yoshitake Masuda

Doctoral Dissertation

**Patterning of TiO₂ Thin Films and Particles
using Self-assembled Monolayers**

Yoshitake Masuda

Department of Applied Chemistry
Graduate School of Engineering
Nagoya University
Nagoya, Japan

December, 2003

Abstract

We have proposed novel methods for site-selective deposition of thin films using self-assembled monolayers (SAMs) and fabricated nano/micropatterns of them in environmentally friendly conditions. We also proposed novel self-assembly processes to fabricate patterns of particle assembly and realized precise arrangement of particles using SAMs. Molecular interface recognitions between functional groups of SAMs and ion, clusters, functional groups on the surface of nano/micro particles were used to control reactions on the substrates.

Chapter 2 Deposition of TiO₂ thin films using hydrolysis reaction and their site-selective depositions

In chapter 2.3, we succeeded in fabricating micropatterns of titanium dioxide thin films on SAMs (self-assembled monolayers). SAMs of OTS (octadecyltrichloro-silane) were formed on Si wafers, and were modified by UV (Ultra Violet) irradiation using a photomask to generate methyl / silanol-pattern. They were used as templates to deposit titanium dioxide thin films by the use of TDD (titanium dichloride diethoxide). Amorphous films with approximate compositions Ti : O : Cl : C = 1 : 2.2 : 0.17 : 0.37 were selectively deposited on silanol regions. Line width variation of the pattern of an as-deposited film was improved to be well below the electronics design rule, 5 %. Annealing the films at high temperatures (400-600 °C) gave rise to an anatase phase, while the resolution of a micropattern remained unchanged.

In chapter 2.4, TiO₂ thin films were grown on several kinds of SAMs using TC (titanium tetrachloride), TDD (titanium dichloride diethoxide) or TE (titanium tetraethoxide) as a starting material. We discussed the thin film formation mechanism and improvement of feature edge acuity through controlling the reactivity by changing functional groups of starting material and the surface functional groups of SAMs. The deposition of TiO₂ from TC or TDD solution was promoted in the silanol group, and the deposition was suppressed on OTS-SAM. On the other hand, TE was deposited regardless of the type of a surface functional group in the whole area of patterned SAMs. The silanol group which has high hydrophilicity accelerated the growth of TiO₂, and the OTS-SAM which has hydrophobicity suppressed the growth of TiO₂. It is also clarified that the chlorine atom in starting material has high reactivity with silanol groups of SAMs.

In chapter 2.5, we present a novel process to gain selective deposition and generate high-feature edge acuity micropatterns of TiO₂ thin films from a gas phase. SAM of OTS were modified to produce a methyl/silanol-pattern and applied as templates to deposit TiO₂ through the use of TDD. Patterned SAM showed high selectivity for nucleation and growth of TiO₂, plus a feature edge acuity of TiO₂ pattern well below 2.1 %. Moreover, we developed a novel process to realize a two-dimensional arrangement of TiO₂ particles onto a SAM from a gas phase.

Chapter 3 Deposition of TiO₂ thin films using liquid phase deposition method and their site-selective depositions

In chapter 3.3, the nucleation and growth process of anatase TiO₂ on several kinds of SAMs in an aqueous solution has been evaluated in detail. Homogeneously nucleated TiO₂ particles and amino groups of SAM showed negative or positive zeta potential in the solution, respectively. The adhesion of TiO₂ particles to the amino group surface by attractive electrostatic interaction caused rapid growth of TiO₂ thin films in the supersaturated solution at pH 2.8. On the other hand, TiO₂ was deposited on SAMs without the adhesion of TiO₂ particles regardless of the type of SAM in the solution at pH 1.5 whose degree of supersaturation is low due to high concentration of H⁺. Additionally, the orientation of films deposited on all SAMs was shown to be improved by enlarging the reaction time regardless of the kind of SAM or pH. It is conjectured that the adsorption of anions to specific crystal planes caused c-axis orientation of anatase TiO₂.

In chapter 3.4, we have developed a novel method for site-selective deposition (SSD) of thin films using a seed layer. The deposition process of anatase TiO₂ from an aqueous solution was evaluated in detail using a quartz crystal microbalance and it was found that the nucleation and initial growth of anatase TiO₂ were accelerated on amorphous TiO₂ thin films compared with silanol, amino, phenyl or octadecyl groups. Amorphous TiO₂ thin films were deposited on silanol regions of a patterned octadecyltrichlorosilane self-assembled monolayer from a titanium dichloride diethoxide solution. This substrate was immersed in an aqueous solution containing Ti precursor to be used as a template for SSD. Anatase TiO₂ was selectively deposited on amorphous TiO₂ regions to form thin films. Consequently, a micropattern of anatase TiO₂ thin film which had high feature edge acuity was successfully fabricated in an aqueous solution.

In chapter 3.5, site-selective immersion was realized using a SAM which has a pattern of both hydrophilic and hydrophobic surfaces. A solution containing Ti precursor contacted the hydrophilic surface during the experiment and briefly came in contact with the hydrophobic surface via our newly developed method. The solution on the hydrophilic surface was replaced with a fresh solution by continuous movement

of bubbles. Thus TiO_2 was deposited and a thin film was grown on the hydrophilic surface selectively. TiO_2 thin film fabricated by site-selective immersion method has no cracks and the feature edge acuity of its micropattern was much higher than that of the micropattern obtained by the lift-off process.

In chapter 3.6, we proposed a novel method to fabricate nano/micro-scaled patterns of thin films and successfully fabricated patterns of anatase TiO_2 thin films in an aqueous solution at 50°C . 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.

Chapter 4 Particle assembly and patterning

In chapter 4.3, novel processes to arrange fine silica spheres two-dimensionally on SAM were developed. SiO_2 sphere surfaces were modified to have CN groups by the use of trichloroethoxysilane, and CN groups were oxidized to COOH groups with t-BuOK. A SAM of PTCS (phenyltrichlorosilane) was modified to have a phenyl / silanol-group pattern by UV irradiation using a photomask and was used as a template to arrange fine SiO_2 spheres. SiO_2 spheres were selectively attached to silanol surfaces possibly forming ester bonds, which enabled the fabrication of micropatterned arrangements of SiO_2 spheres.

In chapter 4.4, the fabrication of novel micro/nano-sized devices by assembling inorganic particles is anticipated for future microelectronics which will make use of their attractive functions. The surface modification of SAMs was studied to prepare templates for sphere assembly. Phenyl groups of SAM were modified into silanol groups by UV irradiation through a photomask, by applying an electric current using an atomic force microscope (AFM) probe, or by contact pressure with a diamond tip. They were used as templates to arrange fine inorganic particles. In addition to the formation of ester bonds, siloxane bond

formation between spheres and SAMs was also found to be effective for sphere arrangement. Low-dimensional close-packing of SiO₂ spheres was achieved through the formation of siloxane bonds. The two-dimensional arrangement of functional particles on SAMs in a controlled manner through the formation of strong chemical bonds, such as ester bonds or siloxane bonds, can be applied to the microfabrication of ceramic devices.

In chapter 4.5, novel processes to realize low-dimensional arrangement of SiO₂ particles were proposed. Particle wires and a pattern of the close-packed particle monolayer were fabricated in the solution at room temperature. SAMs were formed on Si substrates and modified to be suitable for templates of precise arrangement. Particles were arranged precisely in the desired positions in the solution using well controlled electrostatic interactions and chemical bond formation between particles and substrates.

In chapter 4.6, we developed a novel process to fabricate particle wires through self-assembly on hydrophilic regions of SAMs. An SAM of octadecyltrichlorosilane was formed on a silicon substrate and modified by UV irradiation to create a pattern of hydrophobic octadecyl and hydrophilic silanol groups. Ethanol or water containing particles (550 nm ϕ or 800 nm ϕ) was dropped onto a patterned SAM. The solution was separated into two droplets with a liquid bridge between the droplets along the hydrophilic regions of a patterned SAM. The droplets and the liquid bridge were used as a mold for fabrication of a two-dimensional pattern of colloid crystals. Particle wire was formed between two droplets and colloid crystals such as an opal structure were formed at both ends of the particle wire after drying the solution. The particle wires constructed from a close-packed structure or non-close-packed structure, i.e. square lattice, were fabricated through self-assembly at room temperature using this method.

In chapter 4.7, we developed a novel self-assembly process to fabricate an orderly array of particle wires constructed from a close-packed structure from colloidal solution without preparation of patterned templates. 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 or blocks.

Contents

Abstract

Contents

Chapter 1 Introduction	1
1.1 Background	1
1.2 Thin film fabrications and their patterning	5
1.2.1 Thin film fabrications in the solutions	5
1.2.2 Titanium dioxide thin film	8
1.3 Particle assembly and patterning	12
1.4 References	16
Chapter 2 Deposition of TiO ₂ thin films using hydrolysis reaction and their site-selective depositions	24
2.1 Introduction	24
2.2 Experimental procedure	24
2.3 Site-selective deposition and micropatterning of titanium dioxide thin film on self-assembled monolayers from a solution	26
2.4 Mechanism for site-selective deposition of titanium dioxide on self-assembled monolayers	32
2.5 Site-selective deposition and micropatterning of titanium dioxide on self-assembled monolayers from a gas phase	40
Chapter 3 Deposition of TiO ₂ thin films using liquid phase deposition method and their site-selective depositions	47
3.1 Introduction	47
3.2 Experimental procedure	47
3.3 Site-selective deposition of anatase TiO ₂ thin films in an aqueous solution using a seed layer	51
3.4 Site-selective deposition of anatase TiO ₂ thin films in an aqueous solution by site-selective immersion method	58
3.5 Site-selective deposition of anatase TiO ₂ thin films in an aqueous solution by site-selective elimination method	65
3.6 Deposition mechanism of anatase TiO ₂ on self-assembled monolayers from an aqueous solution	74

Chapter 4 Particle assembly and patterning	86
4.1 Introduction	86
4.2 Experimental procedure	87
4.3 Site-selective deposition of particles to form randomly deposited particle layers using ester bonds formation	88
4.4 Novel surface modifications of SAMs and site-selective deposition of particles to form close-packed particle layers using chemical reactions	97
4.5 Site-selective deposition and precise arrangement of particles in the solution	102
4.6 Site-selective deposition and precise arrangement of particles using a liquid mold and its drying process	110
4.7 Self-assembly fabrication for two-dimensional orderly array of particle wires	116
Chapter 5 Summaries	120
5.1 Thin film fabrication and site-selective deposition	120
5.2 Particle assembly and patterning	123
5.3 Surface modification and patterning of SAM	126
5.4 Discussions of my study in the field of research	126
Chapter 6 General conclusions and Future prospects	127
6.1 General Conclusions	127
6.2 Future prospects	127
List of Achievement	129
Acknowledgements	133