Site-Selective Deposition of Ceramic Thin Films Using Self-Assembled Monolayers

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Site-selective deposition (SSD) of ceramic thin films was proposed to fabricate nano/microstructures of ceramics. Several conceptual processes for SSD using self-assembled monolayers (SAMs) as templates were proposed, and nano/micropatterns of ceramic thin films were successfully fabricated. Molecular recognition of SAMs was effectively used to achieve high site-selectivity. These processes can be used for the fabrication of various ceramic devices under environment-friendly conditions. [Received August 14, 2003; Accepted November 28, 2003]

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1. Introduction

Ceramic thin films have recently been fabricated in solutions without high-temperature sintering in order to reduce energy consumption and allow application for various substrates having low heat resistance. The fabrication of ceramic thin films from solutions has been encouraged by the development of environment-friendly chemistry such as Green & sustainable chemistry,1-6 Bioinspired materials chemistry,7 Biomimetic materials chemistry,7 Soft-solution processing,8-10 Soft chemistry (“Chimie douce” in French),11-12 Liquid phase deposition,13-37 Chemical bath deposition, (CBD)7,13,14,36,37 Electroless deposition (ED) with catalyst,7,13,14,58,63 Successive layer adsorption and reaction (SILAR),7,13,14,64,96 Sol-gel process,97-99, Hydrothermal reaction,99 Electrodeposition,100-103 and so on. Solution processing of ceramics allows us to prepare ceramic thin films on the surface of solids such as substrates, particles, and fibers. Ceramic nano/microstructures can also be fabricated by applying these solution systems to electronic or photonic devices. Many kinds of lithography or patterning techniques have been developed to prepare patterns of thin films, for instance, X-ray/electronbeam lithography and photolithography,104 microcontact printing,105-106 wet etching,107 ink-jet printing,108 embossing,109-110 slip-pressing,111 charge-based printing,112 micromolding,113 and cold welding.114 However, etching or lift-off processes are required in many of these methods, which increases waste and energy consumption, and makes the process complicated. Additionally, etching or lift-off processes cannot be applied to corrosion-resistant ceramics. The deposition of thin films only on desired areas of a substrate is thus required for the patterning of ceramic thin films.

Here, we propose site-selective deposition (SSD)115-117 of ceramic thin films and try to fabricate nano/micropatterns of thin films. Self-assembled monolayer (SAM), which can modify the surface of solids with various functional groups, was used as the template to enable molecular recognition for SSD. Solution systems were developed and applied to SSD of ceramic thin films on patterned SAMs by the proposed novel SSD processes.

2. Strategies for site-selective deposition

Site-selective deposition115-117 of thin films has been achieved and nano/micropatterns of them have been fabricated in our study. We proposed direct SSD of amorphous TiO₂ thin films using hydrolysis reaction,118-123 amorphous Ta₂O₅ thin films using hydrolysis reaction,124 amorphous SnO₂ thin films using hydrolysis reaction,125-128 amorphous TiO₂ thin films using a peroxotitanate complex deposition (PCD) method,129-130 and amorphous SrTiO₃ thin films131-135 (Fig. 1(a)). A patterned SAM of octadecyltrichlorosilane (OTS) which has silanol groups and octadecyl groups was used as a template for the patterning of amorphous TiO₂ thin films. Amorphous TiO₂ was selectively deposited on silanol regions in the titanium dichloride diethoxide (TDD) solution using the hydrolysis reaction of TDD to produce micropatterns of thin films that had high feature edge acuity. TDD can form chemical bonds with silanol groups to form amorphous TiO₂ thin films, but cannot form chemical bonds with octadecyl groups. This difference was used for site-selective deposition. Additionally, the surface of hydrophilic silanol groups has many adsorbed water molecules on it, however, the surface of hydrophobic octadecyl groups has fewer adsorbed water molecules. TDD needs water molecules to hydrolyze and thus amorphous TiO₂ thin films can be formed on silanol regions much faster than on octadecyl regions. Condensation between TDD and silanol groups and between TDD molecules releases water molecules, and this promotes further condensation. These two mechanisms, i.e., the difference in ability to form chemical bonds and the difference in adsorption of water molecules, are essential factors in the site-selectivity of this method.

A catalyst pattern was used for site-selective deposition to prepare micropatterns of ZnO136-138 (Fig. 1(b)). This method uses a catalyst pattern as a template which induces the deposition of thin films. The feature edge acuity of micropattern depends on that of the catalyst pattern, and thus high feature edge acuity of the catalyst pattern leads to high feature edge acuity of the pattern of thin films.

Electrostatic interaction was shown to be used for SSD139-142 (Fig. 1(c)). A patterned SAM having amino groups showing positive zeta potential and silanol groups...
showing negative zeta potential was used as a template. Homogeneously nucleated HAp particles or dispersed Ni particles which show negative zeta potential were adhered on amine groups by electrostatic interaction. This process is simple and effective for the deposition of nano/microparticles. HAp particle layers were further grown to form thin films in the so-
lution. This technique can be used to prepare micropatterns of thin films or particle layers.

Additionally, site-selective elimination\(^{[43]}\) was proposed as shown in Fig. 1 (d). Site-selectivity resulted from the difference in adhesion strength of depositions. The patterned SAM having OTS regions and silanol regions was immersed in a solution containing a Ti precursor and subjected to ultrasonication during the immersion process. 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 against mechanical vibration by ultrasonication. 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 used to fabricate nano/micro-scale patterns in the solution by immersing a substrate that has regions on which depositions adhere strongly and regions on which depositions adhere weakly, enabling elimination by treatment such as ultrasonication.

The concept of SSD using a seed layer\(^{[44]}\) is shown in Fig. 1 (e). 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 its nucleation and initial growth 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 reduce 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.\(^{[118]–[122]}\) 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 fabricated. The concept of SSD using a seed layer is to use a pattern of seed layers as a template which accelerate the deposition of thin films by the formation of nucleation sites, the reduction of nucleation energy, the promotion of film growth or other factors.

Moreover, site-selective immersion\(^{[45]}\) was proposed using a SAM having a pattern of hydrophilic and hydrophobic surfaces (Fig. 1(f)). 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. Site-selectivity in this process results from the difference in solution contact period. Other SSIs were achieved in solutions (Fig. 1 (a–e)), however, site-selective immersion was conducted out of the solution. The immersion times of hydrophilic regions and hydrophobic regions were controlled to produce SSD. Though it is difficult to obtain a pattern having high feature edge acuity with this method, the technique can be used to fabricate any kind of micropattern provided the film can be deposited from a solution.

3. SAM preparation

Self-assembled monolayer (SAM)\(^{[146]–[158]}\) can modify the surface of solids such as a substrate, particles, or fibers with various functional groups. Patterned SAMs were used as templates in our SSD processes to deposit ceramic thin films on desired areas of substrates, and the molecular recognition of functional groups of SAM was the key technique for SSD. An Si wafer (p-type Si [100]) was sonicated in water, ethanol or acetone for 10 min, respectively, and exposed for 2 h to UV light (184.9 nm) (low-pressure mercury lamp, NL–UV253, Nippon Laser & Electronics Lab.) to clean the surface\(^{[156]–[158]}\) (Fig. 2). OTS–SAM and PTCS (phenyltrichlorosilane)-SAM were prepared by immersing the Si substrate in an anhydrous toluene solution containing 1 vol.% OTS or PTCS respectively for 5 min under an N\(_2\) atmosphere. APTS (3-Aminopropytrimethoxysilane)-SAM was prepared by immersing the substrate in an anhydrous toluene solution containing 1 vol.% APTS for 1 h in air. The substrates with SAMs were then baked at 120°C for 5 min to remove residual solvent and to promote chemisorption of the SAM. SAMs were exposed for 2 h to UV light in air with 14.0 hPa relative humidity through a photomask. The UV-irradiated regions became hydrophilic due to the formation of Si–OH groups, while the non-irradiated part remained unchanged. OTS–SAM has a methyl group as the end of the long methylene chain (octadecyl group), and
PTCS-SAM and APTS-SAM have a phenyl group and an amino group, respectively. Initially deposited OTS-SAM, PTCS-SAM and APTS-SAM showed water contact angle of 96°, 74° and 48° measured by a sessile drop method, respectively. UV-irradiated surfaces of SAMs were, however, wetted completely (contact angle < 5°).

4. Nano/micropatterns fabricated by site-selective deposition

The processes for SSD of thin films are shown conceptually in Fig. 1. We proposed several methods for SSD by using many types of interactions between SAMs and solutions. The procedures and mechanisms are discussed in detail in this section.

(a) Direct site-selective deposition\(^{(118)-(135)}\)

We developed novel solution systems to deposit uniform amorphous TiO\(_2\) or SnO\(_2\) thin films. SSDs of thin films were proposed using these solution systems.

(a-1) Direct site-selective deposition of amorphous TiO\(_2\) thin films using hydrolysis reaction of titanium compounds\(^{(118)-(121)}\)

Patterned OTS-SAM was immersed in an anhydrous toluene (99.8%, water <0.002%, Aldrich) solution containing 0.1 M TDD for 30 min under an N\(_2\) atmosphere using a glove box. All glassware was dried in a dry box at 50°C before use. The estimated partial pressure of H\(_2\)O in the N\(_2\) atmosphere is below 0.1 hPa. Chlorine atoms of TDD react with H\(_2\)O and change into OH\(^-\), which further react with silanol groups of SAM resulting in the formation of Ti-O-Si bonds\(^{(159)}\). The ethoxy group, O\(_2\)CH\(_2\), of TDD is hydrolyzed into hydroxyl groups which are further condensed to form Ti-O-Ti bonds.\(^{(159)}\) The thickness of films can be easily controlled by varying the soaking time. After SAM substrates had been rinsed with toluene and preserved in air, thin films appeared on the silanol surfaces of OTS-SAM but were not observed on octadecyl surfaces\(^{(114)}\). A micropattern of amorphous TiO\(_2\) thin films was thus fabricated on a patterned OTS-SAM. Line width measurements at 15 equally spaced points on each line indicated an average printed line width of 23.3 μm. Line edge roughness, as measured by the standard deviation of the line width, was ~0.5 μm, representing a ~2.1% variation (i.e., 0.5/23.2) in the nominal line width.\(^{(118)}\) X-ray diffraction measurements (XRD) (Rigaku RU-200) with CuK\(_\alpha\) radiation (40 kV, 30 mA) for as-deposited thin films showed that they were composed of amorphous phases. The ratio of oxygen to titanium was evaluated after 20 min of Ar\(^+\) ion sputtering to avoid the influence of the contaminated layer on the surface. The 1s peak of O can be deconvoluted into two curves (ratio of 529.7 eV (films) and 531.3 eV (silicon oxide) is 1 : 0.22). The ratio of oxygen to titanium was estimated to be 2.2 : 1. Small amounts of chlorine and carbon were also detected (Ti : O : Cl : C = 1 : 2.2 : 0.17 : 0.37).\(^{(118)}\)

(b) Direct site-selective deposition of amorphous SnO\(_2\) thin films\(^{(125)-(128)}\)

Current research activity in gas sensing material is directed toward building new micro-sensor-system onto one chip where the micro sensing devices with highly selective response abilities to the specific inflammable and toxic gases in air are integrated at the predefined sites. SnO\(_2\) is a typical n-type semiconductor gas sensor, and has been mostly noticed among almost all gas sensing devices in the industrial field since the semiconductor gas sensors were first reported in 1962, due to its high-sensitivity to every flammable and toxic gases, low-cost, fast response speed, high chemical stability, and low power consumption. The gravest disadvantage in current SnO\(_2\) bulk ceramic and thick film sensors is a poor selectivity to the detectable gas species. In the improvement of this disadvantage, one of the most effective techniques is to control thickness of SnO\(_2\) thin film.

We show herein a novel technique for fabricating the micropatterning of SnO\(_2\) film with different thickness ranging between several nanometers to sub-micrometers.

For the specially regulated film growth, a patterned methyl-terminated organosilane self-assembled monolayer (MOSAM) was employed as a template. Different precursors, such as SnCl\(_4\) (TC), C\(_6\)H\(_{12}\)SnCl\(_3\) (BTT), SnCl\(_2\)-2H\(_2\)O (TCH) were used as a starting materials. The patterned MOSAMs were immersed into TC, BTT, and TCH solutions.

Sn-based thin films were deposited on silanol-areas in the patterned MOSAMs using hydrolysis reactions of TC, BTT, and TCH in the solvents, respectively. Figure 4 shows an example of the micropatterned growth of ultrathin tin hydroxide film from BTT solution. The black contrast shows an as-deposited film on silanol area, while the white contrast means no film growth occurred on methyl-terminated area, due to the hydrophilic-hydrophobic anti-interaction. Interestingly, the film growth rate in TC solution was about 6 times faster than that in BTT. This is due to the generation of hydrophobic surface after the certain immersion time. This behavior was quantitatively investigated by quartz crystal microbalance measurement. In BTT and TC solutions, the film thickness could be precisely controlled with site-selectivity below 100 nm. On the other hand, film growth rate in TCH solution was enormously larger than that in BTT or TC solution. Of particular importance is that as-deposited SnO\(_2\) thin film obtained in TCH solution was composed of the fine SnO\(_2\) particles,

![Fig. 3. SEM micrographs of a micropattern of amorphous TiO\(_2\) thin films deposited from the solution using the hydrolysis reaction of titanium compound.](image-url)
whose configuration is suitable for gas sensing material. The SnO₂ thin film with the thickness of sub-micrometer was precisely fabricated by this aqueous solution processing. X-ray photoelectron microscopic analysis verified that no Sn component deposited on methyl-terminated area. The solution technique introduced here is capable of depositing other metal oxide films with desirable thickness onto monolayer template formed on the substrate.

(a–3) Direct site-selective deposition of amorphous TiO₂ thin films using a peroxotitanate complex deposition (PCD) method[29–130].

We developed a novel environment-friendly aqueous solution system to deposit amorphous TiO₂ thin films at room temperature (Fig. 5). H₂TiO₃ (3 g, 80%, Mitsuwa) was added to an ice-cooled solvent consisting of H₂O₂ (25 cm³, 30% in H₂O, Mitsubishi) and ammonia (5 cm³, 25% in H₂O, Kishida). After stirring for 90 min, a homogenous pale yellow-green solution was obtained. This homogeneous solution was then diluted with deionized water (> 18 MΩ cm) to 5 mM Ti⁴⁺ at pH 1.9–2.0 (adjusted by the addition of an appropriate amount of HNO₃). Patterned PTS–SAM was then floated on the surface of the diluted solution with the SAM surface upside down at room temperature (~24°C or 37°C) for 1–120 h to deposit a thin film. The large contrast between octadecyl regions and silanol regions suggested successful selective deposition of TiO₂ film on the silanol regions. The selectivity was further confirmed on the basis of enlarged photographs of the silanol regions and octadecyl regions; a dense film was formed on the silanol regions by coalescence of closely packed particles, compared to some fragmentary white grains that formed on the octadecyl regions. The selectivity, film morphology, thickness, fundamental dielectric properties and growth mechanism were further investigated. The results suggested that the present method is a promising alternative for site-selective deposition of TiO₂ thin films through a low-temperature, environment-friendly process.

(a–4) Direct site-selective deposition of amorphous TiO₂ thin films from a gas phase[122–123]

Furthermore, patterns of thin films were fabricated from a gas phase by direct SSD using hydrolysis reaction of TDD. Patterned OTS–SAM and a TDD solution were placed in an airtight container in an N₂ atmosphere instead of oxygen and kept at 90°C for 2 h. Thin films were confirmed to have formed on silanol regions but not on octadecyl surfaces. These films did not peel off under sonication in acetone and showed strong adhesion to the substrate, showing that silanol groups have high selectivity for heterogeneous nucleation and TiO₂ growth of thin films as observed by SEM.[124] Many islands of deposited TiO₂ were observed on the silanol surface at the onset of film formation.[125] Films formed via island particle growth and coalescence. A small number of TiO₂ particles generated by bulk nucleation were observed on TiO₂ thin films deposited from TDD liquid solution, but none were detected by SEM on the thin films deposited from a gas phase in an N₂ atmosphere. The line edge roughness was estimated to be ~2.1% and the feature edge acuity of a titanium dioxide pattern can be improved by using a higher feature edge acuity photo-mask.

(a–5) Direct site-selective deposition of amorphous SrTiO₃ thin films[131–135]

We have succeeded in direct SSD of double oxide thin films such as SrTiO₃ (STO) on patterned SAMs by the liquid phase deposition (LPD) method (Fig. 6). SAMs of heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilanes [HFDTS,
CF$_3$(CF$_2$)$_7$(CH$_2$)$_5$SiCl$_3$ were prepared on Si wafers and modified by UV irradiation through a photomask. This SAM template was composed of HFDT$_2$ surfaces (Si(CH$_2$)$_2$(CF$_2$)$_7$CF$_3$) and silanol surfaces. The patterned SAM-covered substrate was then immersed in an (NH$_4$)$_2$TiF$_6$/Sr(NO$_3$)$_2$/H$_3$BO$_3$ aqueous solution at 50°C to deposit a solid phase. (NH$_4$)$_2$TiF$_6$, which could form [Ti(OH)$_2$F$_{x-n}$]$_2^2$ slowly in an aqueous solution, was selected as a source of TiO$_2^2$. H$_3$BO$_3$ is a scavenger of fluoride and was used to control the reaction rate. The STO films were selectively deposited in the silanol regions. The as-deposited film was amorphous and contained fluoride as the main impurity. With annealing at 500°C for 2 h in air, the as-deposited film was crystallized into SrTiO$_3$ and the fluorine was eliminated. Film morphology was characterized by both SEM and AFM. Metal-oxide-semiconductor (MOS) devices were prepared by using an as-deposited film or a crystallized film as a gate oxide. The dielectric constant of SrTiO$_3$ thin films and the leakage current of the MOS device were evaluated. These results indicate that the SrTiO$_3$ film fabricated by a combination of the SAM technique with LPD method through a one-step process is promising for application to dielectric films.

(b) Catalytic site-selective deposition$^{136-138}$

We fabricated micropatterns of ZnO on a pattern of catalyst to induce the deposition of ZnO (Fig. 7). A photopatterned SAM with phenyl/OH surface functional groups was used as the template. ZnO micropatterns deposited from an aqueous solution at 55°C showed patterned cathodoluminescence images (Fig. 7). The selective, electroless deposition of ZnO was achieved on a Pd catalyst that had been adhered to the phenyl surfaces only.

Prior to the deposition of ZnO, catalyst particles were selectively attached to the phenyl groups of the substrate. The substrate was initially immersed in an NaCl based Pd/Sn colloid (Cataposit 44, Shipley), which contained $1.8 \times 10^{-3}$ M PdCl$_2$ and $4.2 \times 10^{-2}$ M SnCl$_2$, and then in an acidic solution of HBF$_3$ (Accelerator 19, Shipley). It is also possible to selectively attach other catalysts, such as when an HCl based colloid (Catalyst 6F, Shipley) or an NaCl based product prepared as described in the patent literature$^{140}$ is used. For the electroless deposition of ZnO, the SAM substrate was soaked in an aqueous solution of Zn(NO$_3$)$_2$ (0.05 M) and dimethylamine borane (DMAB) (0.01 M) at 55°C for 30 min. The solution of zinc nitrate and DMAB was transparent during the reaction, and hence deposition occurred via heterogeneous nucleation on the Pd catalyst particles attached to the substrate. X-ray diffraction revealed that the deposits were randomly oriented polycrystalline ZnO.

Micropatterns of ZnO were observed by SEM. The ZnO deposits consisted of particles about 0.2 μm in diameter. The finest line-pattern obtained by this method was 1 μm wide. Ideally, it should be possible to draw lines as fine as the particle size by the present deposition method. The edge roughness feature was estimated as several times that of the particle size; the edge acuity was thus comparable to the recent success with TiO$_2$ on a patterned SAM.$^{115}$ After the surfaces with attached catalysts were fully covered with ZnO (in less than 15 min), no more ZnO particles grew with further soaking, probably because ZnO cannot act as a self-catalyst (as happens in the case of electroless plating of Cu).

Cathodoluminescence (CL) was measured at RT with an electron beam at an excitation voltage of 5 kV and current of 200 pA.$^{141}$ The spectra measured on the phenyl and OH surfaces are illustrated in Fig. 7(d). Broad visible light lumines-

![Fig. 6. SEM micrograph of a micropattern of amorphous SrTiO$_3$ thin films.](image)

![Fig. 7. (a, b) Monochromatic 600 nm CL image for the patterned ZnO: (a) 1 μm wide lines; (b) Large feature size area. (c) Line profiling of the 600 nm CL intensity along the line indicated in (b). (d) Cathodoluminescence (CL) spectra measured from the phenyl and OH surfaces. Visible light luminescence (500 ± 800 nm) was observed only from the ZnO deposited phenyl surface regions.](image)
cence (500~800 nm) was observed (even without post-annealing) only at the ZnO-deposited regions on the phenyl surfaces. Luminescence of the wavelength longer than that of usual green emission (530 nm) implies that the present sample contained some defects,\(^{162,163}\) which must have been introduced during the deposition carried out under the low-temperature, aqueous conditions. We confirmed that neither the Pd catalyst nor the PTCS SAM showed luminescence. Figure 7(a, b) shows monochromatic CL images of 600 nm resolved from the same area as shown in SEM micrographs. The resolution was good enough to obtain virtually the same images as for the SEM images, except that the images looked a little blurred, due to excitation by secondary electrons from neighbors. Figure 7(c) shows the CL intensity profile along the line indicated in Fig. 7(b). This suggests that each particulate film of a micropattern is relatively homogeneous, showing only a small fluctuation in luminescence intensity.

(c) Site-selective deposition using electrostatic interaction\(^{139-142}\)

Electrostatic interaction was used for SSD of particles to form patterns of thin films.

(c-1) Site-selective deposition of HAp particles by electrostatic interaction\(^{139-141}\)

Hydroxyapatite (HAp) microparticles were generated at 50 °C in the simulated body fluid (SBF) with high supersaturation degree (1.5 SBF; the concentrations of Ca\(^{2+}\) and PO\(_4^{3-}\) alone are 1.5 times that in 1.0 SBF) buffered carefully at pH 7.6~7.7. Zeta potential of HAp microparticles was shown to be negative in the solution and decreased from ~11.5 mV to neutrality owing to the absorption of cations accompanied by the simultaneous growth of microparticles. APTS-SAM was modified by UV irradiation to have a pattern of regions of amino groups and regions of silanol groups. The patterned SAM was immersed in the solution containing HAp particles to be used as a template. Amino groups showed positive zeta potential, whereas silanol groups showed negative zeta potential in water. Consequently, HAp microparticles selectively adhered on the regions of amino groups by electrostatic interaction (Fig. 8(a)). We could thus achieve SSD by controlling the zeta potential of particles and SAMs.

(c-2) Site-selective deposition of Ni particles by electrostatic interaction\(^{142}\)

Electrostatic interaction was further used for SSD of metal particles such as nickel on ceramic green sheets (Fig. 8(b)). The concept of electrostatic interaction was the same as that which we used in the patterning of HAp, however, the notable development in this study was the surface modification of ceramic green sheets. We studied the surface modification of ceramic BaTiO\(_3\) green sheets including polyvinylbutyral (PVB) as an organic binder and successfully fabricated a patterned SAM which had a region of amino groups and a region of silanol groups on the green sheet. BaTiO\(_3\) green sheets include BaTiO\(_3\) particles and a small amount of PVB as an organic binder. PVB which thinly covers BaTiO\(_3\) particles has no hydrophilic functional groups such as OH groups, and thus the initial BaTiO\(_3\) green sheets show high hydrophobicity (water contact angle of 45°). SAMs were not formed on the initial BaTiO\(_3\) green sheets because APTS molecules cannot form chemical bonds with PVB molecules. The BaTiO\(_3\) green sheet was exposed to UV light for 10 h to photooxidize or remove the PVB coating from the BaTiO\(_3\) particles. OH groups on the BaTiO\(_3\) particles and OH groups produced by photooxidation of PVB can form chemical bonds with APTS molecules. APTS-SAM was prepared by the immersion of a green sheet in APTS solution and was irradiated through a photo-mask to prepare a patterned SAM. The patterned SAM was then immersed in water containing Ni particles that show negative zeta potential in water. Ni particles were attracted to the amino groups of the patterned SAM that show positive zeta potential by attractive electrostatic interaction. Consequently, a micropattern of Ni particles was achieved using a SAM at room temperature in water. This process can be used to fabricate a thin uniform internal Ni electrode for miniaturized high-performance multilayer ceramic capacitors (MLCC).

(d) Site-selective elimination\(^{143}\)

The elimination of deposited particles and heterogeneously nucleated particles on a substrate was shown to be used for patterning (Fig. 9). The concept of this method is to selectively eliminate small depositions from desired areas during the deposition process. The patterned SAM having OTS regions

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**Fig. 9.** AFM image of the pattern of anatase TiO\(_2\) thin films on OTS/OH-patterned SAM fabricated by LPD using ultrasonication at 50°C.

**Fig. 8.** SEM micrographs of a micropattern of (a) HAp and (b) Ni particles.
and silanol regions was immersed in a solution containing a Ti precursor and subjected to ultrasonication for several hours. The difference in adhesion of thin films on substrates was employed for the site-selective elimination. 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. 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, which is the essence of the site-selectivity of this method. The site-selective elimination method can be used to fabricate nano/micro-scaled patterns in the solution by 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.

(e) Site-selective deposition using a seed layer\(^{144}\)

The concept of SSD using a seed layer which accelerates the deposition of thin films was proposed. The deposition process of anatase TiO$_2$ 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 TiO$_2$ were accelerated on amorphous TiO$_2$ thin films compared with silanol, amino, phenyl, or octadecyl groups. Amorphous TiO$_2$ thin films were deposited on silanol regions of a patterned OTS-SAM (Fig. 10 (1-a, b)) from a TDD solution (Fig. 10 (2-a, b)). This substrate was immersed in an aqueous solution containing a Ti precursor at pH 1.5 for 1 h to be used as a template for SSD. Anatase TiO$_2$ was selectively deposited on amorphous TiO$_2$ regions to form thin films. Consequently, a micropattern of anatase TiO$_2$ thin film which had high feature edge acuity was successfully fabricated in an aqueous solution (Fig. 10 (3-a, b)). The center of the anatase TiO$_2$ thin film region was 61 nm higher than the octadecyl regions, and the thickness of the anatase TiO$_2$ thin film was estimated to be 36 nm considering the thickness of amorphous TiO$_2$ thin film (27 nm)\(^{118}\) and OTS molecules (2.4 nm).\(^{144}\) This result is similar to that estimated by QCM measurement (36 nm). The AFM image showed the film roughness to be 3.7 nm (horizontal distance between measurement points: 6.0 $\mu$m), which is less than that of amorphous TiO$_2$ thin film (RMS 9.7 nm, 27 nm thick, horizontal distance between measurement points: 6.0 $\mu$m).\(^{118}\) Additionally, the roughness of the octadecyl group regions was shown to be 0.63 nm (horizontal distance between measurement points: 1.8 $\mu$m).\(^{144}\) This study showed the good performance of the SSD process using a seed layer and the importance of quantitative analysis of the deposition process.

(f) Site-selective immersion\(^{145}\)

The site-selectivity of this method results from the difference in contact time of solution between hydrophilic regions and hydrophobic regions (Fig. 11). The method is based on the simple fact that thin films can be formed on a substrate in solution, however, films cannot be deposited on a substrate which is not immersed in solution. Patterned SAMs which have a pattern of both hydrophilic and hydrophobic surfaces were placed upside down 5 mm above the solution surface. The top clear layer of the solution containing 0.05 M (NH$_4$)$_2$TiF$_4$ and 0.15 M (H$_2$BO$_3$)$_2$ kept at pH 2.8 and 50°C was used for this experiment. Dried air was passed for 4 h through a tube by a pump (Air pump HIBLOW SPP-6EBS, 100 V, 8.5 W, Takatsu Denki Co., Ltd.) 20 mm below the surface of the solution. Bubbles several millimeters in diameter were generated and moved on the surface of a patterned SAM. The solution was repelled and moved quickly on the hydrophobic

Fig. 10. SEM micrographs of (1-a), (1-b) patterned OTS-SAM, (2-a), (2-b) a micropattern of amorphous TiO$_2$ thin films and (3-a), (3-b) a micropattern of anatase TiO$_2$ thin films deposited at pH = 1.5.

Fig. 11. SEM micrographs of micropatterns of TiO$_2$ thin films on HFDTS/OH-patterned SAM fabricated by site-selective immersion.
surface, whereas the hydrophilic surface was wetted by the solution. The solution remaining on the hydrophilic surface was replaced with a new solution by moving bubbles. Consequently, the hydrophilic surface was continuously wetted with the solution, whereas the hydrophobic surface was covered with the solution for only a short time. TiO₂ was deposited on the hydrophilic surface from the solution but not on its hydrophobic counterpart. Thus, site-selective immersion was attained and the difference in immersion time caused site-selective deposition of TiO₂ thin film. This simple process can be applied to other solution systems to form micropatterns of thin films.

5. Summary

SSD has been proposed based on scientific knowledge obtained from investigations of interactions and chemical reactions between functional groups of SAMs and ions, clusters and homogeneously nucleated particles in solutions. Mechanisms and site-selectivities for SSD were further discussed. Our proposals and investigations will contribute to the development of SSD for the fabrication of nano/micropatterns of thin films. This study also showed the good performance of environment-friendly chemistry such as Green & Sustainable Chemistry for the fabrication of nano/microdevices.

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