

## Chapter 2

### Deposition of TiO<sub>2</sub> thin films using hydrolysis reaction and their site-selective depositions

#### 2.1 Introduction

Novel process to realize site-selective deposition of thin films has been required for future nano/micro devices. Additionally, nano/micro-patterns of thin films should be fabricated in environmentally friendly conditions. We proposed novel processes for site-selective deposition of amorphous TiO<sub>2</sub> thin films using hydrolysis reaction of titanium compounds. TiO<sub>2</sub> thin films can be deposited on desired regions of patterned SAMs in the solution. We also realized site-selective deposition of amorphous TiO<sub>2</sub> thin films from a gas phase. Furthermore, deposition mechanism and interaction between titanium compounds and SAMs were investigated in details.

In chapter 2.3, Novel process was proposed to realize site-selective deposition of TiO<sub>2</sub> thin films on a patterned SAM using hydrolysis reaction of titanium compound. In chapter 2.4, deposition mechanism of TiO<sub>2</sub> from titanium compounds was studied on several kinds of functional groups. In chapter 2.5, novel process was proposed to realize site-selective deposition of amorphous TiO<sub>2</sub> thin films from a gas phase.

#### 2.2 Experimental procedure

##### SAM preparation.

OTS-SAM and PTCS (phenyltrichlorosilane) -SAM were prepared by immersing the Si substrate (P-type Si (100)) into an anhydrous toluene solution containing 1 vol% OTS or PTCS respectively for 5 min under a N<sub>2</sub> atmosphere.<sup>25-28</sup> APTS (3-Aminopropyltriethoxysilane) -SAM was prepared by immersing into 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 (184.9 nm) (NL-UV253, Nippon Laser & Electronics Lab.) in air with 14.0 hPa relative humidity through a mesh for transmission electron microscopy. The UV-irradiated regions became hydrophilic due to Si-OH group formation, while the non-irradiated part remained unchanged. OTS-SAM has a methyl group for the end of long methylene chain, 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 °).

#### **Formation of TiO<sub>2</sub> thin films in a solution.**

Patterned SAMs (OTS, PTCS and APTS) were immersed into an anhydrous toluene (99.8 %, water < 0.002 %, Aldrich) solution containing 0.1M TC (titanium tetrachloride) for 3 min, or 0.1M TDD for 30 min, or 0.1M TE (titanium tetraethoxide) for 3 h 30 min (Fig. 1). These experiments were carried out at room temperature under a N<sub>2</sub> atmosphere (99.99 %, water < 550 ppb). Titanium compounds (TC, TDD or TE) react with silanol groups of the SAM and H<sub>2</sub>O molecules which are adsorbed on SAMs and / or remain in the solution. TiO<sub>2</sub> was then formed by the hydrolysis and condensation of titanium compounds (TC, TDD or TE). TiO<sub>2</sub> was deposited on the whole area of large silanol surfaces (each 20 mm × 20 mm) to boost the detection strength of X-ray photoelectron spectroscopy (XPS; ESCALAB 210, VG Scientific Ltd., 1-3 × 10<sup>-7</sup> Pa, measurement area; 3 mm × 4 mm). The X-ray source (MgK $\alpha$ , 1253.6 eV) was operated at 15 kV and 18 mA. Deposited thin films were sputtered in argon for 20 min to purge surface contamination of carbon. These contaminations make our estimation of chemical composition difficult. Standardization was achieved using the C 1s (284.6 eV). Thin films were further evaluated by an X-ray diffractometer (Rigaku RAD-C) with CuK $\alpha$  radiation (40kV, 30mA) with Ni filter and a graphite monochromator. Thickness of the films was estimated by an atomic force microscope (AFM; Nanoscope E, Digital Instruments) and an ellipsometer.

#### **Hydrolysis of TDD and formation of TiO<sub>2</sub> thin films from a gas phase.**

Patterned SAM substrates of OTS and an anhydrous toluene solution containing 0.1M TDD were placed in an airtight Pyrex container in both air and N<sub>2</sub> atmospheres and kept at 90 °C for 2 h, the temperature selected for optimal TDD evaporation. TDD molecules evaporated and diffused to a patterned OTS-SAM surface. TDD chlorine atoms react as H<sub>2</sub>O transmutes to OH, and further react with silanol groups of SAM, resulting in the formation of Ti-O-Si bonds<sup>18</sup>. Ti-O-Ti bonds are formed by chlorine hydrolysis; in addition, a film grows. To control supersaturation by partial H<sub>2</sub>O pressure revision, experiments were conducted in air and N<sub>2</sub> atmospheres. Estimated partial H<sub>2</sub>O pressure in air and an N<sub>2</sub> atmospheres was 14.0 hPa and below 0.1 hPa, respectively.

## 2.3 Site-selective deposition and micropatterning of titanium dioxide thin film on self-assembled monolayers from a solution

Novel process was proposed to realize site-selective deposition of TiO<sub>2</sub> thin films on a patterned SAM using hydrolysis reaction of titanium compound.

### Selective deposition and micropatterning of TiO<sub>2</sub> on SAM

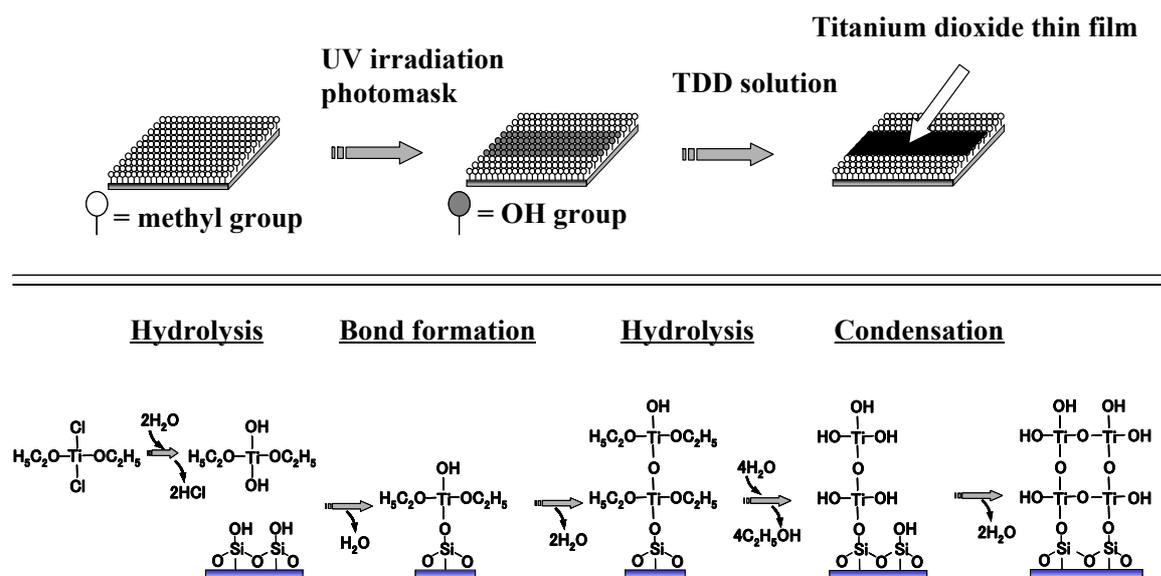


Figure 1. Conceptual process for selective deposition of titanium oxide thin film using a self-assembled monolayer.

Patterned SAM substrates of OTS were immersed into an anhydrous toluene (99.8 %, water < 0.002 %, Aldrich) solution containing 0.1M TDD (titanium dichloride diethoxide) for 5 - 30 min under a N<sub>2</sub> atmosphere using a glove box (Fig. 1). In the case experiments were done in an air, many particles were homogeneously nucleated in TDD solution and they adsorbed on deposited thin films. It shows that elimination of traces of water is important to fabricate high quality thin films. All glass ware were dried in a dry box at 50 °C before use. Estimated partial pressure of H<sub>2</sub>O in a N<sub>2</sub> atmosphere is below 0.1 hPa. Both titanium chloride and titanium alkoxide are known to form chemical bonds with silanol groups, however, the fact that the reactivity of silicon chloride is higher than that of silicon alkoxide, namely Si-Cl > Si-F > Si-OCH<sub>3</sub> > Si-OC<sub>2</sub>H<sub>5</sub> > Si-OC<sub>3</sub>H<sub>7</sub> > Si-OC<sub>4</sub>H<sub>9</sub><sup>1,2</sup> would firmly suggest that Ti-Cl would have higher reactivity than Ti-OC<sub>2</sub>H<sub>5</sub>. Accordingly, chlorine atoms of TDD react with H<sub>2</sub>O changing into OH which further react with silanol groups of SAM resulting in the formation of Ti-O-Si bonds.<sup>3</sup> Ethoxy groups, OC<sub>2</sub>H<sub>5</sub>, of TDD is hydrolyzed into hydroxyl groups which are further condensed to form Ti-O-Ti bonds.<sup>3</sup>

Thickness of films can be easily controlled by soaking time, because chlorine atoms react with silanol groups quickly to form a few molecular layers and ethoxy groups hydrolyze gradually. After SAM substrates were rinsed with toluene and preserved in air, blue thin films appeared on silanol surfaces of OTS-SAM but were not observed on methyl surfaces. Micropattern of a thin film was thus successfully fabricated on patterned OTS-SAM.

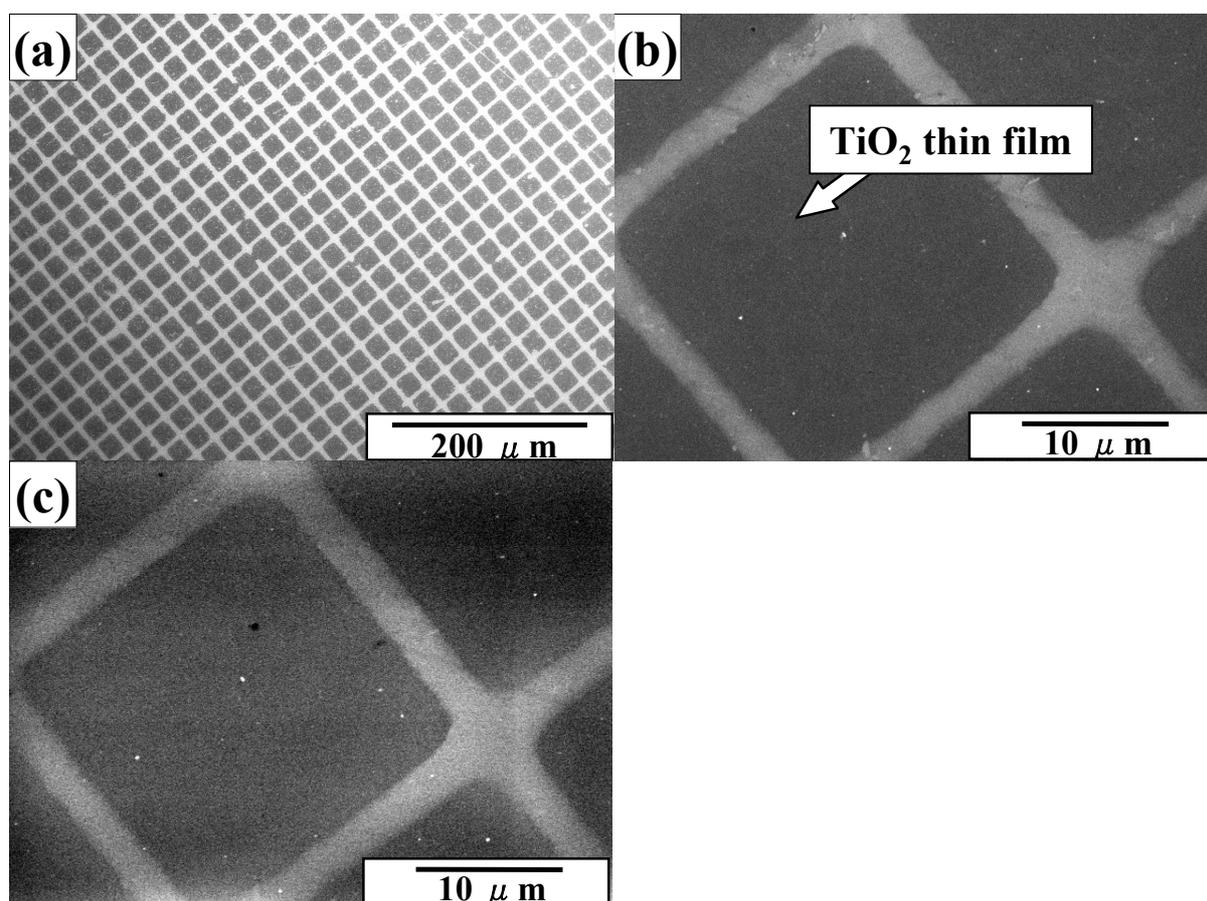


Figure 2. SEM photographs of (a) a micropattern of as-deposited thin films (30 min soaking), (b) magnified area of (a), and (c) after annealing of (b) at 600 °C for 3 h.

Selective deposition of thin films on OTS-SAM was confirmed by scanning electron microscope (S-3000N, Hitachi Ltd.) observation (Fig. 2, 3). These films were not peeled off during sonication in acetone, and showed strong adhesion to the substrate. The line edge roughness was estimated with the same manner as we used for titanium dioxide films fabricated with a liquid phase deposition process.<sup>4</sup> Line width measurements at 15 equally spaced points on each line in Fig. 2 (b) indicate an average printed line width of 23.3 μm. Line edge roughness, as measured by the standard deviation of the line width, is ~ 0.5 μm. This represents an ~ 2.1 % variation (i.e., 0.5 / 23.2) in the nominal line width. This variation is much better than

that of the pattern fabricated with a liquid phase deposition process<sup>4</sup> and the usual 5 % variation afforded by current electronics design rules. This variation is similar to that of a TEM (transmission electron microscopy) mesh (2.1 %) we used for Fig. 2. Therefore, variation of titanium dioxide pattern can be improved through the use of a high resolution photomask. Titanium dioxide wire shown in Fig. 3 was fabricated using a high resolution photomask. The line width variation of this pattern is well below 2.1 %. These observations firmly indicate that micropatterns of titanium dioxide were successfully fabricated using OTS-SAM. OTS-SAM is suitable for selective deposition of a film, because only silanol groups react with TDD and methyl groups inhibit deposition of a film.

Thickness of films was evaluated by an atomic force microscope (Nanoscope E, Digital Instruments). Films obtained after soaking for 5 min and 30 min were 6.9 nm and 27.4 nm thick, respectively. Energy dispersive X-ray analysis (EDAX Falcon, EDAX Co. Ltd.) indicated that thin films consisted of titanium, oxygen and a small amount of chlorine (Ti : Cl = 1 : 0.1) as shown in Fig. 3. Thin films are considered to be of titanium dioxide from this observation.

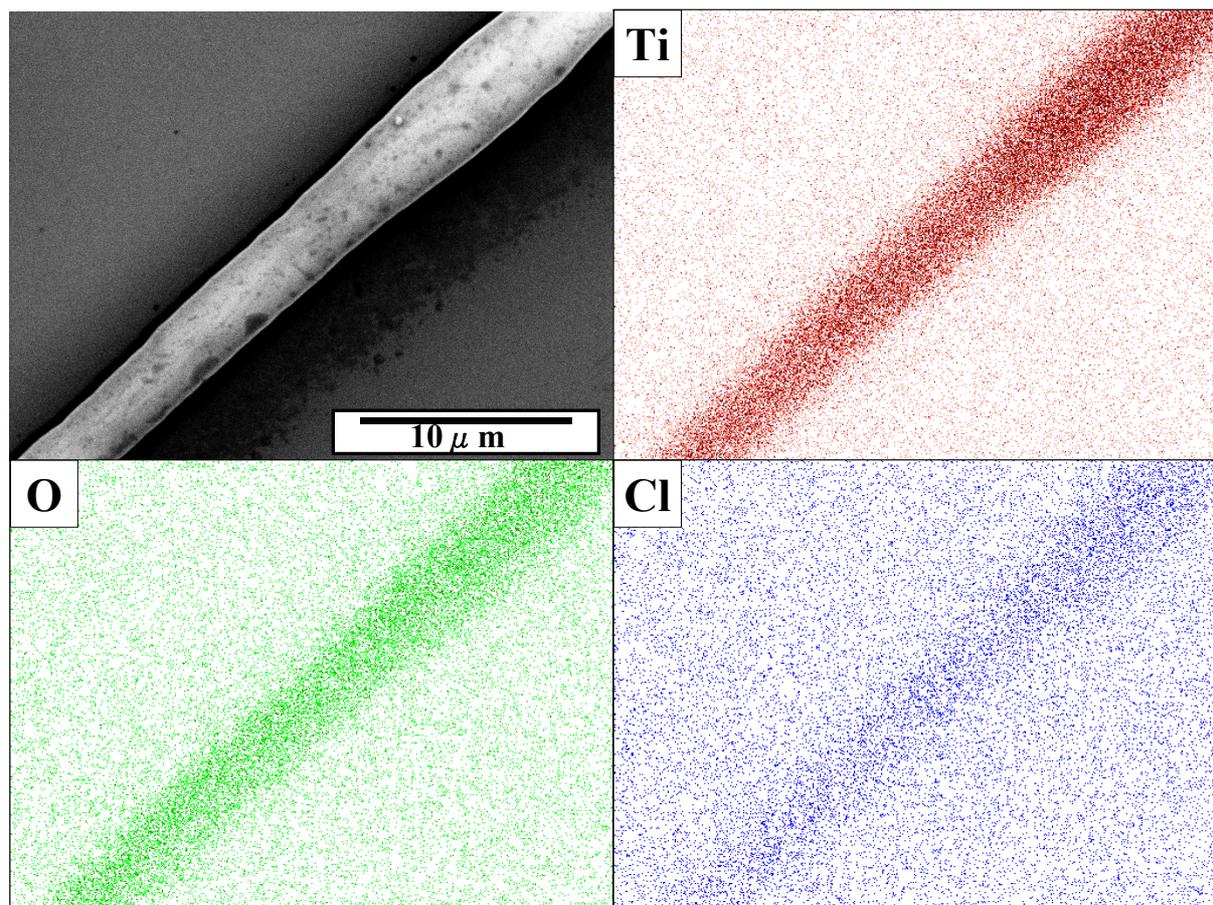


Figure 3. EDX analysis of titanium dioxide micro wire on OTS-SAM ; (a) SEM image and characteristic X-ray images of (b) Ti, (c) O and (d) Cl.

Thin films were further evaluated by XPS (x-ray photoelectron spectroscopy, ESCALAB 210, VG Scientific Ltd.,  $1-3 \times 10^{-7}$  Pa). The x-ray source ( $\text{MgK}\alpha$ , 1253.6 eV) was operated at 15 kV and 18 mA. The spectral peaks corresponding to Ti 2p (458.5 eV) were observed from thin films deposited on the silanol region (Fig. 4). This binding energy is higher than that of Ti metal (454.0 eV), TiC (454.6 eV), TiO (455.0 eV), TiN (455.7 eV) and  $\text{Ti}_2\text{O}_3$  (456.7 eV), and similar to that of  $\text{TiO}_2$  (458.4 - 458.7 eV).<sup>5,6</sup> This suggests the titanium atoms in thin films are positively charged relative to that of titanium metal by formation of direct bonds with oxygen. On the other hand, this spectrum was not observed from methyl regions.

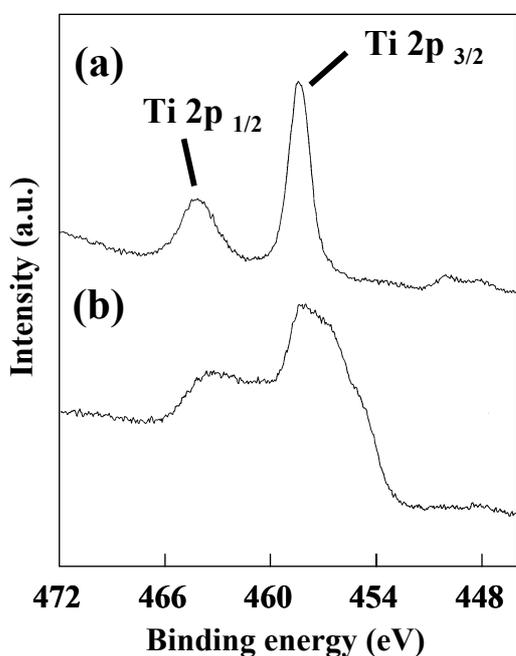


Figure 4. XPS spectra of Ti 2p for titanium oxide thin film formed on the silanol region of OTS-SAM (30 min soaking) (a) before and (b) after  $\text{Ar}^+$  sputtering.

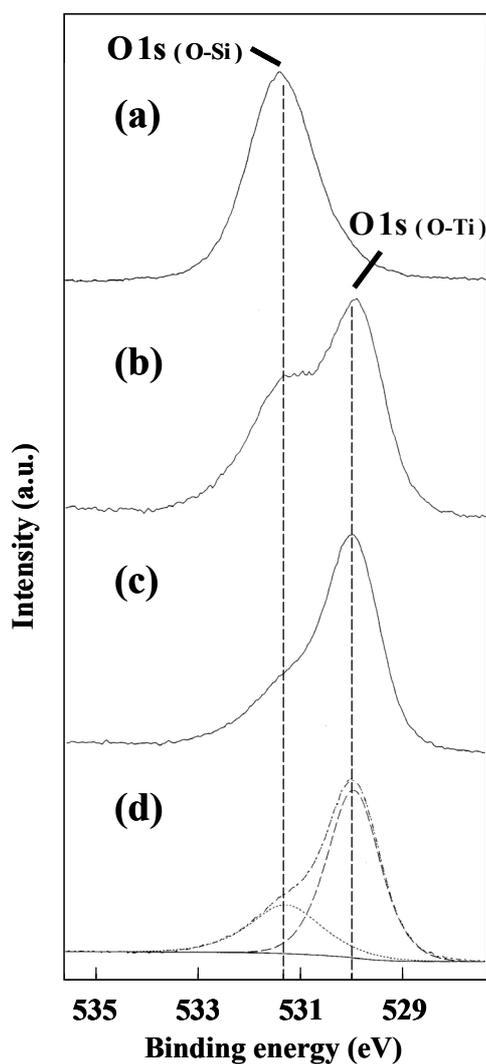


Figure 5. XPS spectra of O 1s ; (a) methyl region of OTS-SAM, (b) thin film formed on silanol region (5 min soaking), (c) thin film formed on the silanol region (30 min soaking), and (d) after  $\text{Ar}^+$  sputtering of (c).

OTS-SAM surfaces showed O 1s (531.3eV) which can be assigned to a silicon oxide layer on the surface of silicon wafer (532.0eV<sup>5</sup>) (Fig. 5 (a)). O 1s peak centered at 530.1 eV was observed from thin films deposited on silanol regions (Fig. 5 (b)), and not observed from methyl regions. The intensity of this peak increased with soaking time (Fig. 5 (c)) and was not observed from methyl regions even after soaking for 30 min. Hence, the peak (530.1 eV) was assigned to the deposited film. This binding energy is similar to that of TiO<sub>2</sub> (529.9 eV<sup>6</sup>, 530.1 eV<sup>5</sup>), and it showed oxygen is negatively charged compared to neutral oxygen molecules (531.0 eV) possibly through the formation of direct bonds with Ti.

The ratio of oxygen to titanium was evaluated after 20 min of Ar<sup>+</sup> ion sputtering to avoid the influence of a contaminated layer on the surface (Fig. 4 (b), Fig. 5 (d)). O 1s peak 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 as 2.2 : 1. Additionally, small amounts of chlorine and carbon were also detected (Ti : O : Cl : C = 1 : 2.2 : 0.17 : 0.37), but the spectral peaks corresponding to C and Cl disappeared after annealing at 400 °C.

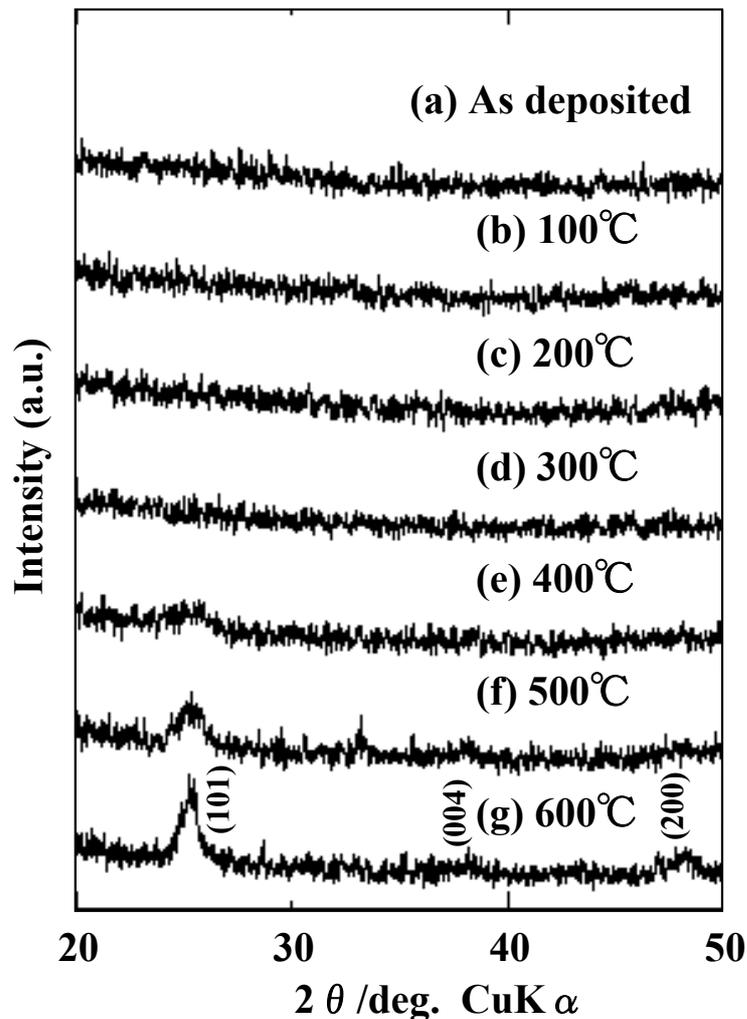


Figure 6. XRD patterns of thin films changing with the change in annealing temperature.

X-ray diffraction measurements (Rigaku RU-200) with  $\text{CuK}\alpha$  radiation (40kV, 30mA) for as-deposited thin films showed that they are composed of amorphous phases (Fig. 6). Heat treatment of the films has demonstrated that amorphous phase converts into crystalline anatase phase above  $\sim 400\text{ }^\circ\text{C}$  and its crystallinity becomes better with higher annealing temperature. The anatase phase further transforms into rutile and / or other phases by annealing above  $1000\text{ }^\circ\text{C}$ . Additional peaks of  $\text{SiO}_2$  were also observed after annealing at  $1000\text{ }^\circ\text{C}$  possibly due to the oxidation of a Si substrate itself.

After annealing a micropattern of titanium dioxide shown in Fig. 2 at  $600\text{ }^\circ\text{C}$  for 3 h, no crack was observed by SEM or AFM (atomic force microscopy), and the resolution of this pattern remained almost unchanged (Fig. 2(c)). These results suggest that high resolution micropatterns of anatase-type  $\text{TiO}_2$  can be fabricated by our newly developed patterning and heat treatment process.

## Conclusions

We succeeded in fabricating micropatterns of titanium dioxide thin films on SAMs. SAMs of OTS were formed on Si wafers, and were modified by UV 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. Amorphous films with approximate compositions  $\text{Ti} : \text{O} : \text{Cl} : \text{C} = 1 : 2.2 : 0.17 : 0.37$  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 ( $400 - 600\text{ }^\circ\text{C}$ ) gave rise to an anatase phase, while the resolution of a micropattern remained unchanged.

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## 2.4 Mechanism for site-selective deposition of titanium dioxide on self-assembled monolayers

Deposition mechanism of  $\text{TiO}_2$  from titanium compounds was studied on several kinds of functional groups.

**Patterning of SAM.** Patterned SAMs (Fig. 1) were observed with a scanning electron microscope (SEM; S-3000N, Hitachi Ltd.), and silanol regions showed white contrast in SEM photographs (Fig. 2 (a-0), (b-0), (c-0)) compared with non-UV irradiated regions. SEM photographs shown in Figure 2 were taken with the same contrast and brightness mode. Patterned APTS-SAM showed highest contrast in these patterned SAMs. This difference is possibly associated with their surface charge. Zeta potentials measured in aqueous solutions (pH=7.0), which should have close relationships with the surface charge present in vacuum, for the surface of silicon substrate covered with silanol groups, phenyl groups (PTCS) and amino groups (APTS) are  $-38.23$  mV,  $+0.63$  mV and  $+22.0$  mV<sup>1</sup>, respectively. Positively charged surface shows black contrast and negatively charged surface shows white contrast in a SEM photograph.

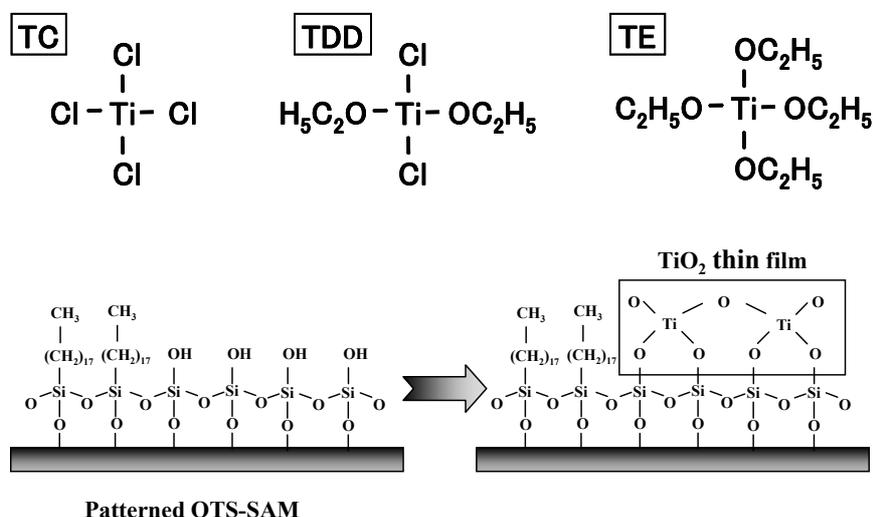


Figure 1. Conceptual process for selective deposition of titanium oxide thin film using self-assembled monolayers.

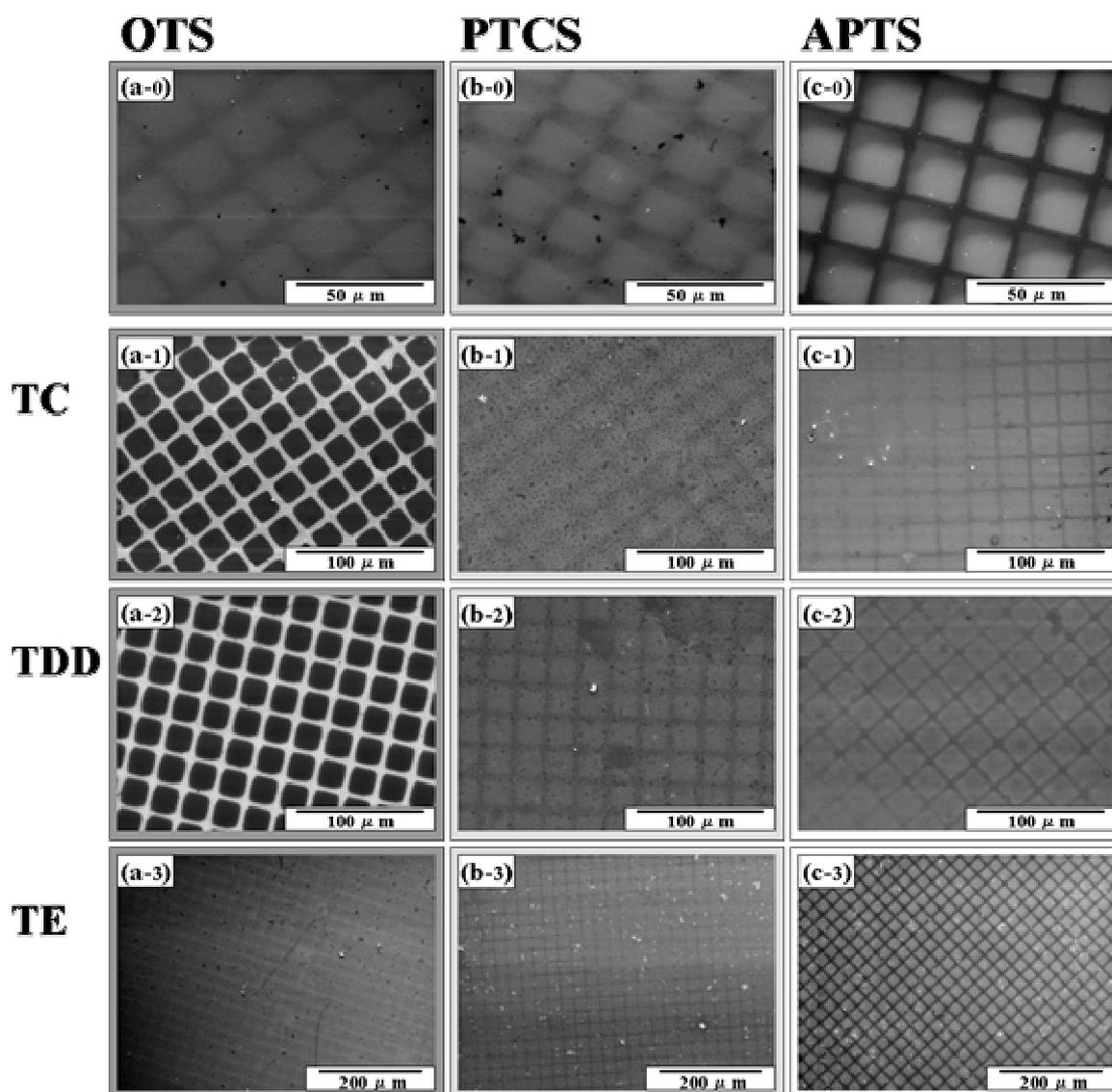


Figure 2. SEM photographs of OTS-SAMs patterned by UV irradiation before (a-0) and after immersing in a TC solution (a-1), a TDD solution (a-2) or a TE solution (a-3), and PTCS-SAMs patterned by UV irradiation before (b-0) and after immersing in a TC solution (b-1), a TDD solution (b-2) or a TE solution (b-3), and APTS-SAMs patterned by UV irradiation before (c-0) and after immersing in a TC solution (c-1), a TDD solution (c-2) or a TE solution (c-3).

**Site-selective deposition of TiO<sub>2</sub> thin films.** After having been immersed in the solution, the patterned-SAMs were observed with a SEM. Selective deposition of TiO<sub>2</sub> was accomplished by a combination of TC and patterned OTS-SAM, and a combination of TDD and patterned OTS-SAM (Fig. 2 (a-1), (a-2)). Thin films of TiO<sub>2</sub> were formed in silanol regions, and the deposition of TiO<sub>2</sub> was suppressed well in OTS-SAM regions for these two combinations. Films deposited in silanol regions showed black

contrast in SEM photographs. These films did not peel off by sonication in acetone and showed strong adhesion to the substrate. On the other hand, thin films were deposited on the whole area of a patterned PTCS-SAM and a patterned APTS-SAM, when TC or TDD was used (Fig. 2 (b-1), (b-2), (c-1), (c-2)). Additionally, thin films were deposited on the whole area of patterned SAMs and many particles were observed on the whole area of SAMs when TE was used (Fig. 2 (a-3), (b-3), (c-3)). Each molecule of TC, TDD and TE has four chlorine atoms, two chlorine atoms and two ethoxy groups, and four ethoxy groups, respectively. Growth rate of the film in silanol regions increased with increasing quantity of chlorine atoms in titanium compounds (growth rate: 12 nm/min [TC], 0.9 nm/min [TDD], 0.14 nm/min [TE]).

Thin films on phenyl groups (PTCS) or amino groups (APTS) deposited from TC or TDD peeled off by sonication in acetone because these thin films don't have strong chemical bonds with SAMs. Micropattern of TiO<sub>2</sub> thin film was thus fabricated by sonication of TiO<sub>2</sub> thin films deposited on a phenyl / silanol patterned SAM or an amino / silanol patterned SAM. However, feature edge acuity of these patterns is much lower than that of the pattern deposited on OTS / silanol patterned SAM because of their lift-off process.

Chlorine atoms in TC or TDD seem to have high reactivity with H<sub>2</sub>O molecules adsorbed on silanol groups compared with ethoxy groups. Accordingly, TiO<sub>2</sub> thin films are formed from TC and TDD in silanol regions through their hydrolysis with H<sub>2</sub>O molecules adsorbed on silanol groups. Thin films are formed in a short time before TC or TDD reacts with H<sub>2</sub>O molecules in the solution to form TiO<sub>2</sub> particles. In contrast, TE molecules which have no chlorine atoms can't easily react with H<sub>2</sub>O molecules adsorbed on silanol groups, but they hydrolyze and condense with H<sub>2</sub>O molecules in the solution to form TiO<sub>2</sub> particles. TiO<sub>2</sub> particles generated in the solution are then adsorbed on the whole area of patterned SAMs. These observations show it is necessary to use a titanium compound which has chlorine atoms to deposit uniform thin films in silanol regions.

Though the deposition of TiO<sub>2</sub> from TC or TDD was sufficiently suppressed by OTS-SAM, it was not suppressed well in the case of PTCS-SAM or APTS-SAM. OTS-SAM has the highest hydrophobicity among these SAMs, and there would be little adsorbed water on OTS-SAM compared with PTCS-SAM or APTS-SAM<sup>2-3</sup>. The water molecule is indispensable for the generation of TiO<sub>2</sub>, but the hydrophobicity of an OTS-SAM seems to suppress the gathering of water molecules and hence prohibits the hydrolysis of Ti-containing molecules to form TiO<sub>2</sub> films. Accordingly, the pattern of highly hydrophilic surface and highly hydrophobic surface appears to be suitable for the site-selective deposition.

Furthermore, OTS-SAMs are known to form films in which interactions between methylene chains for adjacent OTS species, combined with tilting of the chains, produce well-packed films in which the chains

insulate any unreacted underlying silanols from contact with the external solution. OTS-SAM could block any underlying silanols present from reaction with the solution titanium precursors, inhibiting nonselective TiO<sub>2</sub> deposition. Likewise, strong association of water at amino groups of APTS-SAM can provide locally high levels of water required to form TiO<sub>2</sub> from the solution titanium precursors at these sites, leading to more nonselective deposition of TiO<sub>2</sub> in this SAM. In the PTCS-SAM, previous research has shown that chemisorption occurs in a random, disordered fashion to produce more loosely packed SAMs<sup>4</sup>. More recently, it has been observed that aromatic SAMs chemisorbed from aromatic solvent<sup>5-6</sup> form low density SAMs having nanocavities capable of binding adsorbates from solution. Access of titanium precursor to free silanol groups at defect / cavity sites in such aromatic PTCS-SAMs would be one of the reasons of film formation in phenyl groups region.

**Characteristics of micropatterns.** Deposited thin films were further investigated using an atomic force microscope. Surface roughness as evaluated by RMS can be expressed as ;

$$\text{RMS (standard deviation)} = \left[ \frac{\sum_i (Z_i - Z_{\text{ave}})^2}{n} \right]^{1/2}$$

[ Z<sub>i</sub> : height at point “i” (nm), Z<sub>ave</sub> : average of Z (height) (nm), n : number of data points ]

Thin film deposited from TC onto silanol regions was the smoothest (roughness RMS: 2.6 [TC], 9.7 [TDD], 14.0 [TE]) as shown in Fig. 3. It seems to be associated with the quantity of chlorine atoms in titanium compounds. It takes a long time to form a thin film from TE molecule which has no chlorine atoms, and many particles which generated in the solution deposited on the whole area of a substrate. It should be a cause of roughness of the film deposited from TE. The quantity of chlorine atoms in titanium compounds should be maximized to form a smooth thin film.

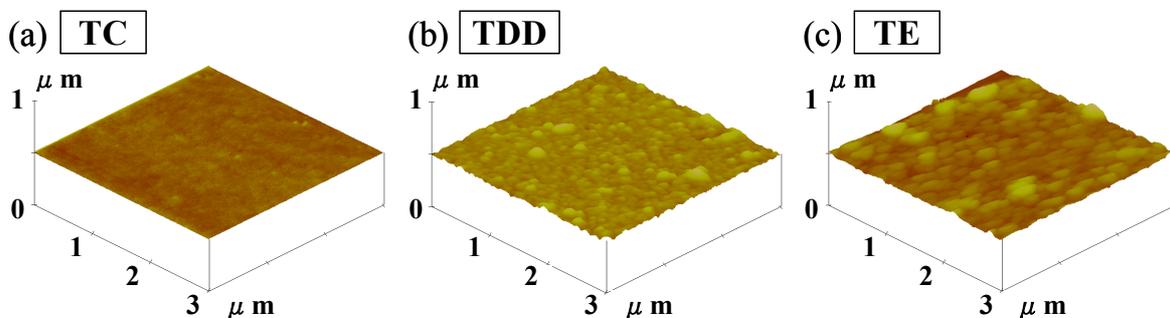


Figure 3. AFM images of thin films deposited from TC (a), TDD (b) or TE (c).

The line edge roughness of these patterns was estimated via the same way used for titanium dioxide films fabricated by a liquid phase deposition process<sup>7</sup>. Line width measurements for the pattern deposited from TDD at 15 equally spaced points on each line revealed an average printed line width of 23.3  $\mu\text{m}$ . Line edge roughness, as gauged by the standard deviation of the line width, was  $\sim 0.5 \mu\text{m}$ , which represents a  $\sim 2.1\%$  variation (i.e.,  $0.5 / 23.2$ ) of nominal line width. This figure far surpasses that for the pattern fabricated in a liquid phase deposition process<sup>7</sup>, exceeding the usual 5% variation afforded by current electronics design rules. Since this variance is similar to that of the TEM mesh (2.1%) we used for Fig. 2, the feature edge acuity of a titanium dioxide pattern can be improved through the use of a higher feature edge acuity photomask. TC molecule also has high selectivity to surface groups, thus the feature edge acuity of the pattern was similar to that of photomask (2.1% variation, (i.e.,  $0.5 / 23.2$ )). It is impossible to discuss the comparative merits of these two molecules (TC and TDD) for the selective deposition, since these molecules showed high selectivity for surface groups and the feature edge acuity of them were the same as that of the photomask.

**Characterization of deposited TiO<sub>2</sub> thin films.** Both titanium and oxygen were confirmed as present in all thin films by XPS. Spectral peaks corresponding to Ti 2p (458.8 eV [TC], 458.5 eV [TDD]<sup>8</sup>, 458.6 eV [TE]) were seen from deposited thin films (Fig. 4, a). This binding energy exceeds that of Ti metal (454.0 eV), TiC (454.6 eV), TiO (455.0 eV), TiN (455.7 eV) or Ti<sub>2</sub>O<sub>3</sub> (456.7 eV), but is similar to that of TiO<sub>2</sub> (458.4 - 458.7 eV)<sup>9-10</sup>, which suggests titanium atoms in thin films are positively charged by forming of direct bonds with oxygen.

The O 1s peak seen from the phase deposited on the silanol surface can be separated into two peaks (Fig. 4, b). Binding energy centered at about 532 eV is similar to that of SiO<sub>2</sub> and significantly decreased by Ar sputtering. These peaks are assigned to natural oxide layer of silicon wafer and contamination on the surface. Binding energy centered at about 530 eV corresponds to that of TiO<sub>2</sub> (530.1eV,<sup>9</sup> 529.9eV<sup>10</sup>). Chemical compositions in molar ratios are estimated from the Ti 2p spectrum, O 1s spectrum [film], C 1s spectrum, and Cl 2p spectrum to be Ti / O / C / Cl = 1 / 2.2 / 0.32 / 0.19 for TC, 1 / 2.2 / 0.37 / 0.17 for TDD, 1 / 1.9 / 0.48 / 0 for TE. A trace of chlorine was detected in thin films deposited from TC or TDD, but not detected in a thin film deposited from TE, since TE molecule has no chlorine atoms. Carbon was detected in the film deposited even from TC, and so the surface of the film must be contaminated with carbon after preparation.

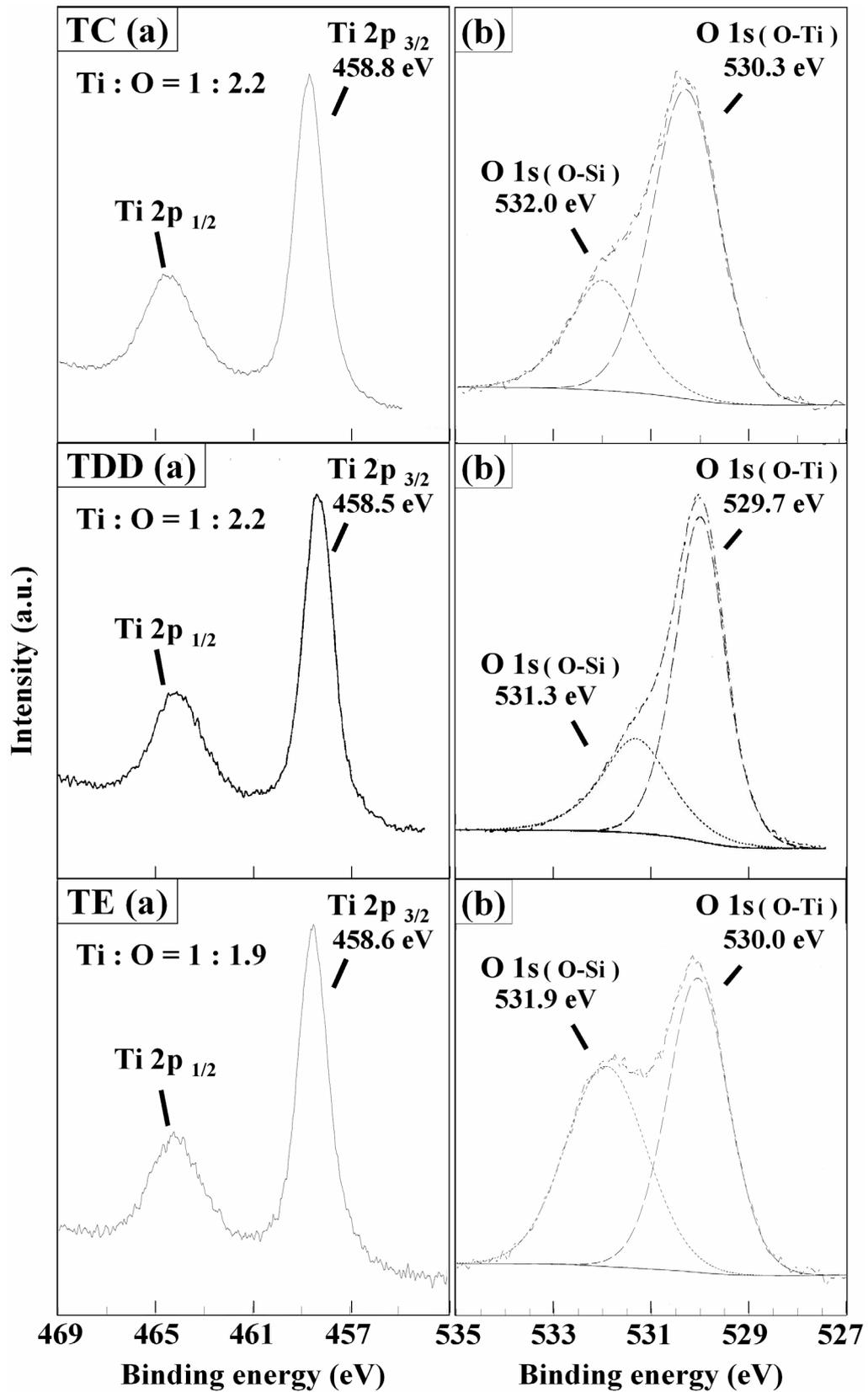


Figure 4. XPS spectra of (a) Ti 2p and (b) O 1s for titanium oxide thin films deposited from TC, TDD or TE.

X-ray diffraction measurements for as-deposited thin films from TC, TDD or TE revealed that they were composed of amorphous phases (Fig. 5). Heat treatment of the  $\text{TiO}_2$  deposited from TC showed that the amorphous phase converts into a crystalline anatase phase above  $\sim 300$  °C. On the other hand, amorphous  $\text{TiO}_2$  deposited from TDD or TE converts into crystalline anatase above  $\sim 400$  °C and its crystallinity improves with higher annealing temperature. The thin films deposited from TC, TDD or TE further transform into rutile and/or other phases by annealing above 1000 °C. Additional peaks of  $\text{SiO}_2$  were also observed after annealing at 1000 °C, possibly due to the oxidation of the Si substrate itself.

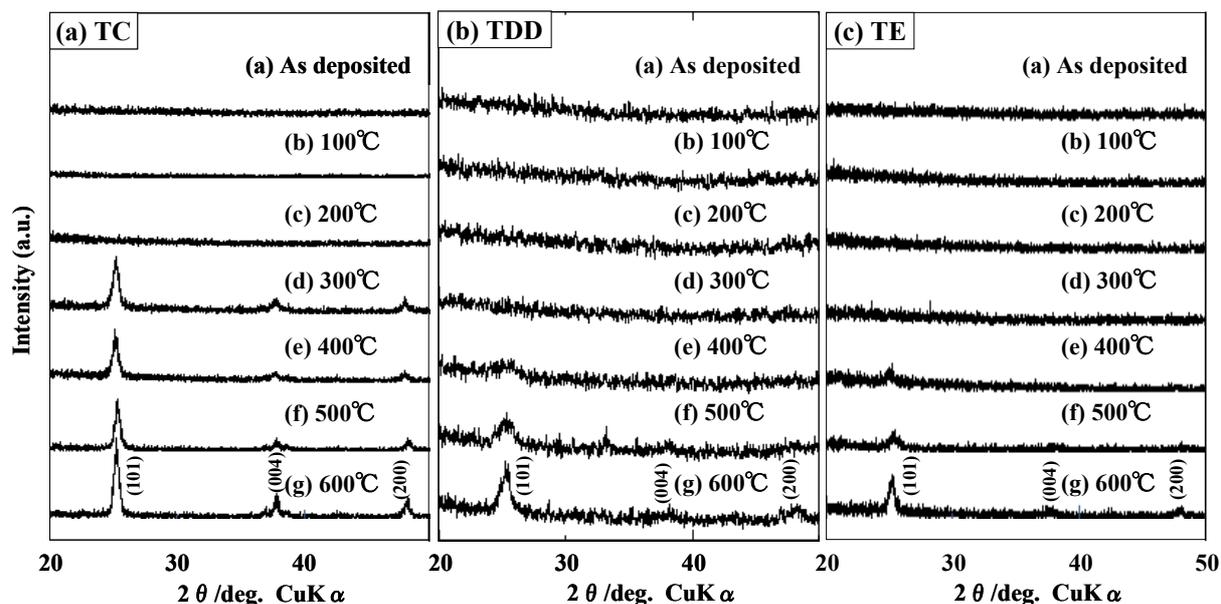


Figure 5. XRD patterns of thin films deposited from (a) TC, (b) TDD or (c) TE changing with the change in annealing temperature.

## Conclusions

$\text{TiO}_2$  thin films were grown on several kinds of SAMs using TDD, TC or TE. The deposition of  $\text{TiO}_2$  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 whole area of patterned SAMs. The silanol group which has high hydrophilicity accelerated the growth of  $\text{TiO}_2$ , and the OTS-SAM which has hydrophobicity suppressed the growth of  $\text{TiO}_2$ . It is also clarified that the chlorine atom in starting material has the high reactivity with silanol groups of SAMs. Growth rate of thin film from TC was the fastest in our experiments, and these films showed very smooth surface. This shows growth rate and quality of thin films can be controlled by the selection of starting materials.

## References

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## 2.5 Site-selective deposition and micropatterning of titanium dioxide on self-assembled monolayers from a gas phase

Novel process was proposed to realize site-selective deposition of amorphous  $\text{TiO}_2$  thin films from a gas phase.

**Micropatterning of  $\text{TiO}_2$  particles.** Patterned SAM substrates of OTS and an anhydrous toluene solution containing 0.1M TDD were placed separately in an airtight container in the air and kept at  $90^\circ\text{C}$  for 2 h (Fig. 1). A scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.) revealed many spherical particles on the whole surface of a patterned OTS-SAM after reaction (Fig. 2, a, b), a significant number of which aggregated (Fig. 2, e). More particles were observed on the bottom of the Pyrex container than at the top. Too, slightly more particles had attached to the silanol regions than to the octadecyl. Surface coverage by the particles in the silanol and octadecyl regions were determined to be 16 % and 10 %, respectively.

Supersaturation in the experiment in air was higher than that in an  $\text{N}_2$  atmosphere. It is considered that very thin  $\text{TiO}_2$  films and/or particles were generated on silanol groups, with small  $\text{TiO}_2$  particles generated in the air first. Minute particles, like clusters of initial nuclei, formed in oxygen are transferred to a silanol surface by convection and gravity and react with  $\text{H}_2\text{O}$  molecules and/or silanol groups, which in turn develop chemical bonds with silanol groups. On the other hand, with the octadecyl surface, tiny particles are carried onto it by convection and gravity, but cannot form chemical bonds with octadecyl groups, since hydrolysis does not occur between particles and these groups. A few particles on the octadecyl surface were then removed by gas convection due to the lack of bonds between particles and the surface. The difference in surface coverage by particles between silanol and octadecyl regions can be associated with dissimilarity in the amount of adsorbed  $\text{H}_2\text{O}$  between the silanol and octadecyl regions.

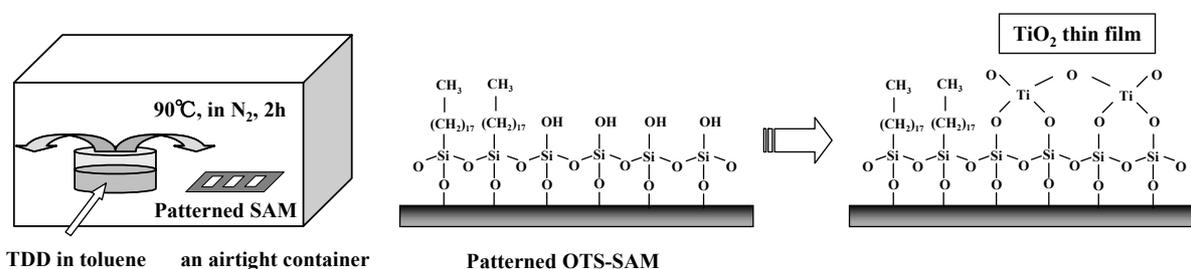


Figure 1. Conceptual process for selective deposition of titanium oxide thin film using a self-assembled monolayer.

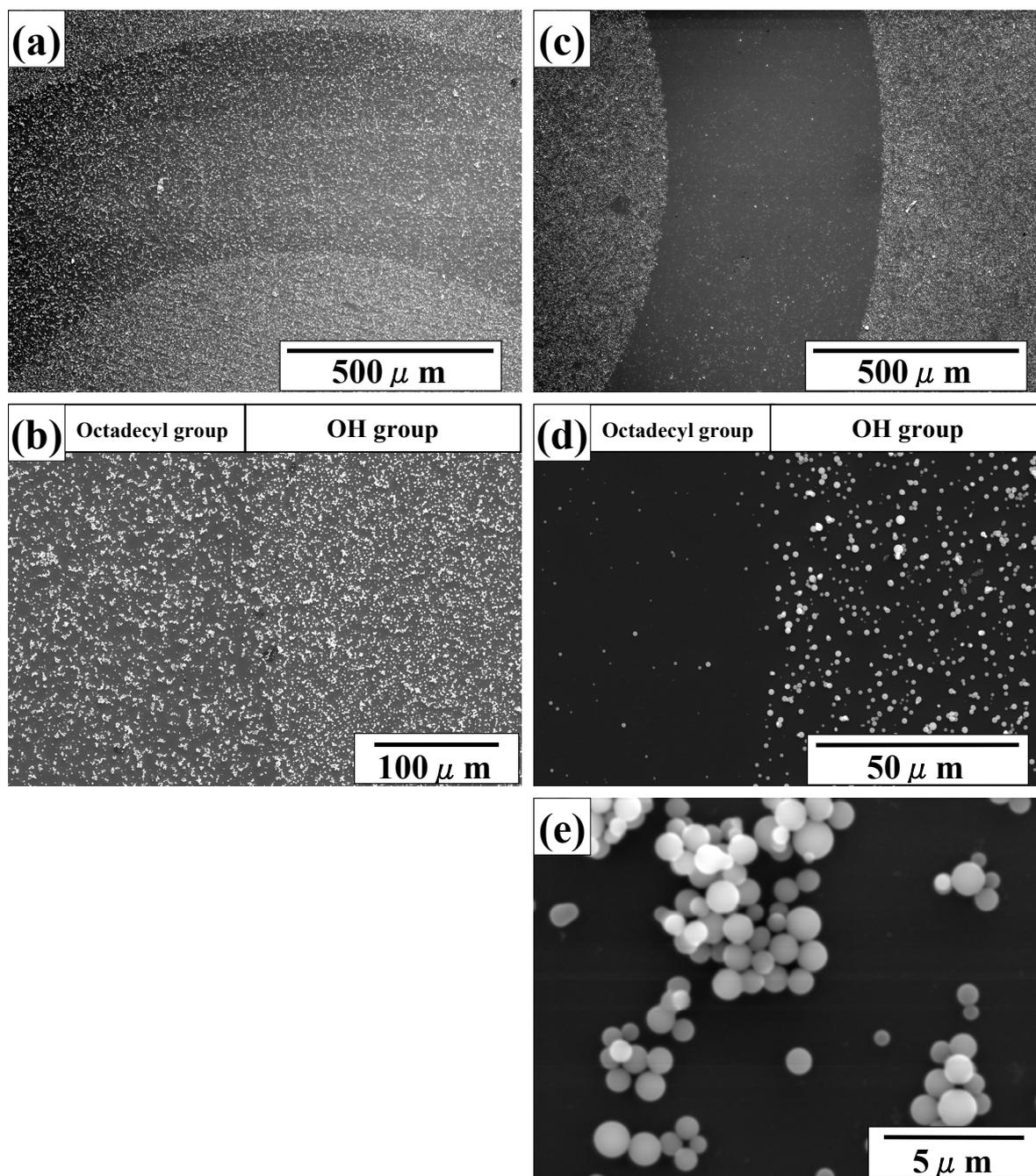


Figure 2. SEM photographs of TiO<sub>2</sub> particles (a, b) before and (c, d) after sonication, and (e) magnified TiO<sub>2</sub> particles.

Water is needed for TDD hydrolysis, and water molecules are adsorbed mainly on the hydrophilic silanol surface rather than that of hydrophobic octadecyl, showing TDD molecules approaching the silanol surface to become hydrolyzed more easily to form  $\text{TiO}_2$  particles. It is presumed that the growth rate of silanol surface particles exceeds that of particles on the octadecyl surface. Also, when the substrate was treated in a sonication bath for 1 min, particles loosely bound to the substrate were removed and surface coverage by particles attached in the silanol and octadecyl regions changed to 9 % and 1 %, respectively (Fig. 2, c, d). Consequently, a two-dimensional selective arrangement of  $\text{TiO}_2$  particles resulted. Sonication treatment revealed that the  $\text{TiO}_2$  particles stick much more firmly to the silanol surface than to the octadecyl, implying that bonding between the nucleating ( $\text{TiO}_2$ ) phase and the silanol surface is far stronger than that occurring on its octadecyl counterpart.

Selective deposition of  $\text{TiO}_2$  particles due to their strong bond with silanol group surfaces is much like the selective deposition of  $\text{SiO}_2$  particles on silanol surfaces as reported recently<sup>1-2</sup>. Moreover, it is proposed that the nucleation of particles and the forming of strong bonds between particles and a SAM can be realized simultaneously in a single process using the present hydrolytic reaction scheme. This method can be applied to the selective deposition of other functional particles to fabricate microdevices.

**Selective deposition of  $\text{TiO}_2$  thin films.** Patterned OTS-SAM and a TDD solution were placed in an airtight container in an  $\text{N}_2$  atmosphere instead of oxygen and kept at 90 °C for 2 h. Thin films were confirmed to have formed on silanol regions but were not on octadecyl surfaces (Fig. 3, a, b). Accordingly, a micropattern of  $\text{TiO}_2$  thin film was successfully fabricated without a lift-off process. These films did not peel off by sonication in acetone and showed strong adhesion to the substrate, showing that silanol groups have high selectivity for heterogeneous nucleation and  $\text{TiO}_2$  growth of thin films as observed by SEM (Fig. 3, d, e, f). Many islands of deposited  $\text{TiO}_2$  were observed on the silanol surface at the onset of film formation and, as seen by the figure. Films formed via island particle growth and coalescence. A small number of  $\text{TiO}_2$  particles generated by bulk nucleation were observed on  $\text{TiO}_2$  thin films deposited from TDD liquid solution,<sup>3</sup> but none were detected by SEM on the thin films deposited from a gas phase in an  $\text{N}_2$  atmosphere. The line edge roughness was estimated via the same way used for titanium dioxide films fabricated in a liquid phase deposition process<sup>4</sup>. Line width measurements at 15 equally spaced points on each line (Fig. 3, b) revealed an average printed line width of 23.3  $\mu\text{m}$ . Line edge roughness, as gauged by the standard deviation of the line width, was  $\sim 0.5 \mu\text{m}$ , which represents a  $\sim 2.1$  % variation (i.e.,  $0.5 / 23.2$ ) of nominal line width. This figure far surpasses that for the pattern fabricated in a liquid phase deposition process<sup>4</sup> exceeds the usual 5 % variation afforded by current electronics design rules, and very nearly

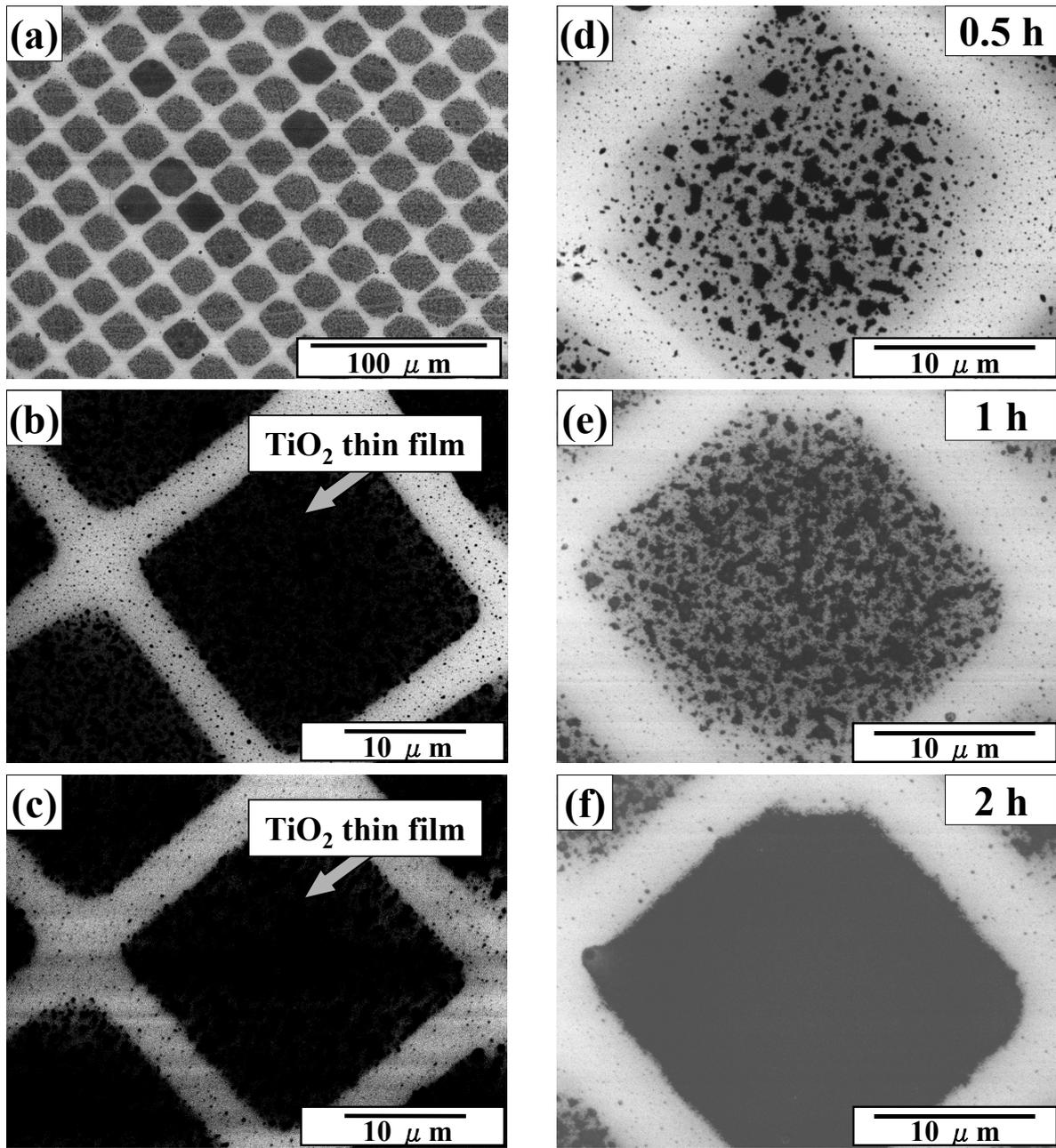


Figure 3. SEM photographs of (a) a micropattern of as-deposited thin films (2 h), (b) magnified area of (a), (c) after annealing of (b) at 600 °C for 3 h, and thin films deposited for (d) 0.5 h, (e) 1 h and (f) 2 h.

equals that of the pattern deposited from a TDD solution<sup>3</sup> Since this variance is similar to that of the TEM mesh (2.1 %) we used for Fig. 3, the feature edge acuity of a titanium dioxide pattern can be improved through the use of a higher feature edge acuity photomask.

The film formation process was further investigated using an atomic force microscope (AFM; Nanoscope E, Digital Instruments). Surface roughness as evaluated by RMS can be expressed:

$$\text{RMS (standard deviation)} = \left[ \sum_1 (Z_i - Z_{\text{ave}})^2 / n \right]^{1/2}$$

$Z_i$  : height at point “i”

$Z_{\text{ave}}$  : average of Z (height)

n : number of data points

Many islands were seen at the start of film formation (Fig. 4, a). Surface roughness decreased with reaction time (roughness RMS: 12.36 [0.5 h], 6.60 [1 h], 3.68 [2 h]), while surface coverage grew with reaction time (coverage: 29 % [0.5 h], 61 % [1 h], 100 % [2 h]). Films obtained after 2h reaction were about 20 nm thick. Average growth rate (10 nm/h) more or less equals sixth of that for the liquid solution process (~ 60 nm/h).<sup>3</sup>

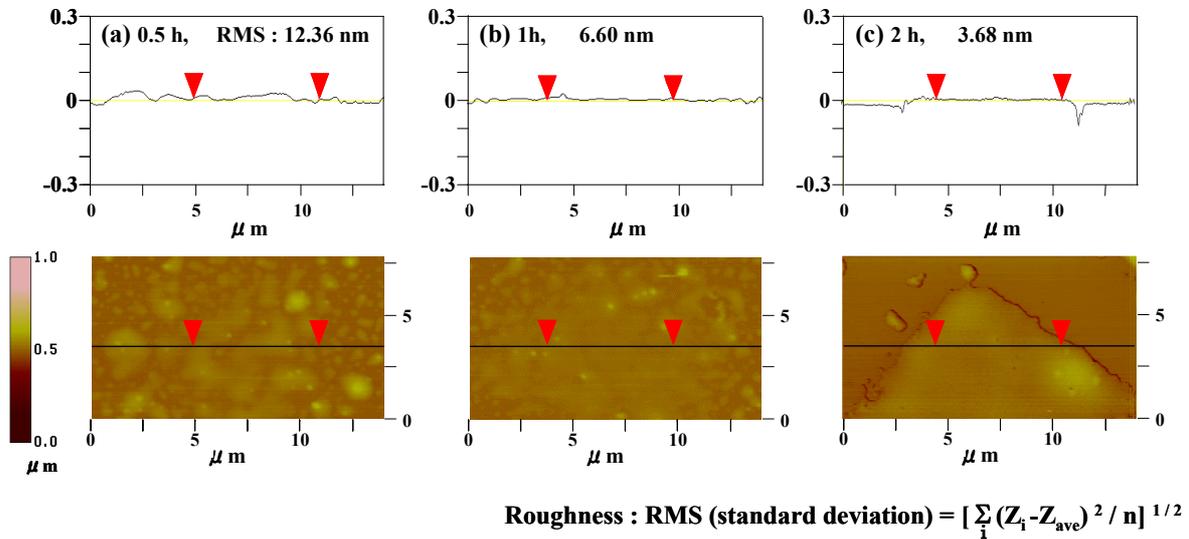


Figure 4. AFM photographs of thin films deposited for (a) 0.5 h, (b) 1 h and (c) 2 h.

**Characterization of deposited TiO<sub>2</sub> thin films.** TiO<sub>2</sub> was deposited on the whole area of large silanol and octadecyl surfaces (each 20 mm × 20 mm) to boost the detection strength of X-ray photoelectron spectroscopy (XPS; ESCALAB 210, VG Scientific Ltd.,  $1-3 \times 10^{-7}$  Pa, measurement area; 3 mm × 4 mm). The X-ray source (MgK $\alpha$ , 1253.6 eV) was operated at 15 kV and 18 mA. A deposited thin film was sputtered in argon for 60 min to purge surface contamination, with electrification corrected by a spectrum (84.0 eV) of deposited Au. Both titanium and oxygen were confirmed as present in the thin films. Spectral peaks corresponding to Ti 2p (459.1 eV) were seen from deposited thin films in the silanol regions (Fig. 5, a). This binding energy exceeds that of Ti metal (454.0 eV), TiC (454.6 eV), TiO (455.0 eV), TiN (455.7 eV) or Ti<sub>2</sub>O<sub>3</sub> (456.7 eV), but is less than that of TiO<sub>2</sub> (458.4 - 458.7 eV)<sup>3,5-6</sup> which suggests titanium atoms in thin films are positively charged relative to those of titanium metal by formation of direct bonds with oxygen. Conversely, this spectrum was not observed from octadecyl regions. The O 1s peak seen from the deposited phase on the silanol surface can be separated into two curves (the ratio of 530.8 eV [film] and 532.5 eV [silicon oxide] is 1 : 0.65) (Fig. 5, b). Binding energy of the film is like that of TiO<sub>2</sub> (530.1 eV,<sup>3,5</sup> 529.9 eV<sup>6</sup>). The ratio of oxygen to titanium was estimated from the Ti 2p spectrum (459.1 eV) and O 1s spectrum (530.8 eV) to be 3.1 : 1, a bit greater than the ratio of TiO<sub>2</sub> deposited from a TDD solution (O : Ti = 2.2 : 1). A trace of carbon was detected, but the chlorine content fell short of the discernment limit (Ti : C = 1 : 0.46). The carbon derived from unreacted molecules and surface contamination not removed by 60 min sputtering.

TiO<sub>2</sub> thin films on UV irradiated OTS-SAM were assessed by a Fourier-transform infrared spectrometer (FT-IR 610, Jasco, Ltd.), with UV-irradiated OTS-SAM used as a reference. The absorption band at 948.8 cm<sup>-1</sup> appearing in the spectrum can be assigned to Ti-O-Si (950 cm<sup>-1</sup>)<sup>7</sup>, indicating that TDD chlorine atoms react with H<sub>2</sub>O changing into the OH groups, which further react with silanol groups of SAM, resulting in the formation of Ti-O-Si bonds.

X-ray diffraction measurements (Rigaku RU-200) with CuK $\alpha$  radiation (40kV, 30mA) for as-deposited particles and thin films revealed them as composed of amorphous phases. Heat treatment of the TiO<sub>2</sub> showed that the amorphous phase converts into crystalline anatase phase above ~ 400 °C and its crystallinity improves with higher annealing temperature. The anatase phase further transforms into rutile and/or other phases by annealing above 1000 °C. Additional peaks of SiO<sub>2</sub> were also observed after annealing at 1000 °C, possibly from oxidation of the Si substrate itself.

After annealing the micropattern of titanium dioxide shown in Fig. 3 at 600 °C for 3 h, no crack was observed by SEM or AFM, and the feature edge acuity of this pattern underwent virtually no change (Fig. 3, c). These results suggest that high-feature edge acuity micropatterns of anatase-type TiO<sub>2</sub> can also be formed by our new patterning and heat treatment process.

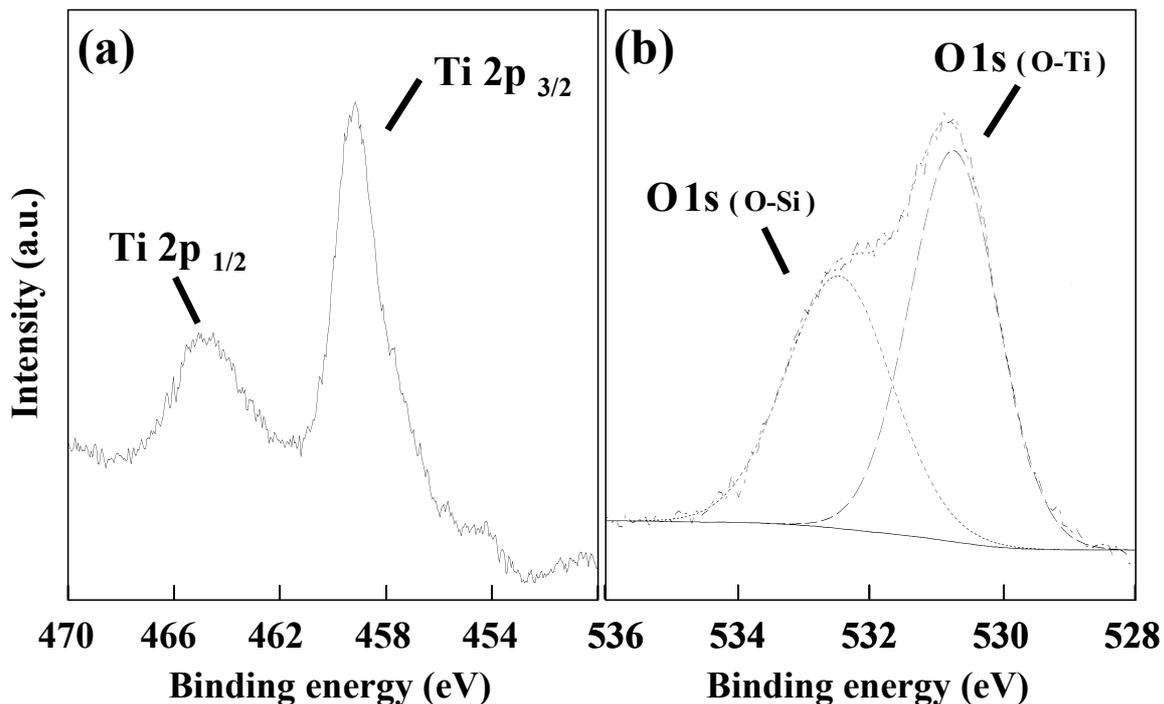


Figure 5. XPS spectra of (a) Ti 2p and (b) O 1s for titanium oxide thin film formed on the silanol region of OTS-SAM.

## Conclusions

TiO<sub>2</sub> thin films were selectively deposited on silanol areas of SAM in an N<sub>2</sub> atmosphere from gas phase. Patterned SAM showed high selectivity for nucleation and TiO<sub>2</sub> growth, hence feature edge acuity of the TiO<sub>2</sub> pattern matched that of a photomask and equals that of the pattern formed in a TDD solution.<sup>3</sup> TiO<sub>2</sub> particles generated by bulk nucleation were observed in a TDD solution<sup>3</sup> and they deteriorate the quality of thin films. Nevertheless, thin films can result only through heterogeneous nucleation from a gas phase. Our gas phase deposition process has an advantage over the liquid phase deposition type for fabricating high quality and high-feature edge acuity micropatterns.

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