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# Site-Selective Deposition of Anatase TiO<sub>2</sub> in an Aqueous Solution Using a Seed Layer

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We have developed a novel method for site-selective deposition (SSD) of thin films using a seed layer. The deposition process of anatase TiO<sub>2</sub> 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<sub>2</sub> were accelerated on amorphous TiO<sub>2</sub> thin films compared with silanol, amino, phenyl, or octadecyl groups. Amorphous TiO<sub>2</sub> 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 TiO<sub>2</sub> was selectively deposited on amorphous TiO<sub>2</sub> regions to form thin films. Consequently, a micropattern of anatase TiO<sub>2</sub> thin film which had high feature edge acuity was successfully fabricated in an aqueous solution.

## Introduction

Titanium dioxide (TiO<sub>2</sub>) thin films are of interest for various applications including microelectronics,<sup>1</sup> optical cells,<sup>2</sup> solar energy conversion,<sup>3</sup> highly efficient catalysts,<sup>4</sup> microorganism photolysis,<sup>5</sup> antifogging and self-cleaning coatings,<sup>6</sup> gratings,<sup>7</sup> gate oxides in MOSFETs (metal-oxide-semiconductor field effect transistors),<sup>8</sup> and photonic crystals.<sup>9</sup> Accordingly, fabrication of thin films and micropatterns of TiO<sub>2</sub> has been attempted by several methods.

Various methods for making TiO<sub>2</sub> films from solutions have been reported.<sup>10–17</sup> Microfabrication using these methods has also been attempted.<sup>18–23</sup> A micropattern of

anatase TiO<sub>2</sub> thin films was fabricated on a patterned self-assembled monolayer (SAM) by the lift-off process.<sup>18</sup> A phenyltrichlorosilane (PTCS) SAM was irradiated by ultraviolet light through a photomask to form a silanol/phenyl micropattern and used as a template. Anatase TiO<sub>2</sub> thin films were deposited on the entire area of a patterned SAM from (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> aqueous solution with the addition of H<sub>3</sub>BO<sub>3</sub> at 50 °C for 6 h. Thin films on phenyl regions were then peeled off by sonication. Thin films on the silanol region showed strong adhesion to silanol groups compared with those on the phenyl regions. Consequently, a micropattern of anatase TiO<sub>2</sub> was fabricated at low temperature. However, the lift-off process degrades the feature edge acuity of the micropattern. A novel process for site-selective deposition (SSD) is required that does not suffer from these drawbacks.

SSD of thin films has been realized and micropatterns of them have been fabricated by several methods. We have reported direct SSD of amorphous TiO<sub>2</sub> thin films<sup>21–23</sup> or ZrO<sub>2</sub> thin films.<sup>24</sup> A patterned SAM<sup>18,25–27</sup> of octadecyltrichlorosilane (OTS) which has silanol groups and octadecyl groups was used as a template. Amorphous TiO<sub>2</sub> was selectively deposited on silanol regions using the hydrolysis reaction of Ti precursors such as titanium dichloride diethoxide (TDD) from TDD solution<sup>21,23</sup> or TDD vapor<sup>22</sup> and produced micropatterns of TiO<sub>2</sub> that had high feature edge acuity. Saito et al.<sup>28,29</sup> fabricated a micropattern of ZnO thin film using a micropattern of catalyst. Pd colloids were selectively adhered to phenyl group regions of a patterned SAM which had silanol groups and phenyl groups. This substrate was then soaked in an aqueous solution of Zn(NO<sub>3</sub>)<sub>2</sub> and dimethylamineborane

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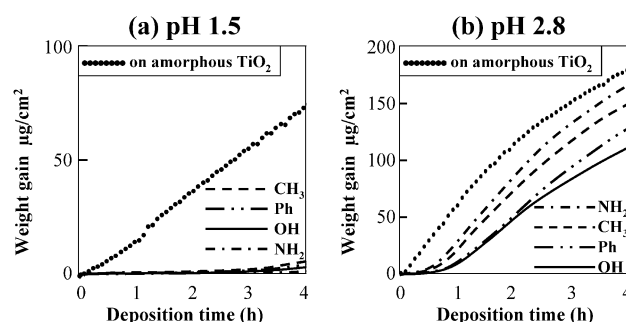
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at 55 °C for 30 min. The rate of chemical reaction to generate ZnO is increased by Pd colloids which act as a catalyst. ZnO particles of about 0.2  $\mu\text{m}$  in diameter were thus selectively deposited on Pd colloid regions to fabricate a micropattern of ZnO thin films. A micropattern of HAp (hydroxyapatite) thin films was fabricated by electrostatic interaction.<sup>30</sup> A patterned SAM of aminopropyltriethoxysilane (APTS) which has amino groups and silanol groups was immersed in an aqueous solution. Negatively charged HAp particles were attracted to positively charged amino groups by static attractive interaction. Particles adhered to the amino groups were further grown to connect with each other and form thin films on regions of amino groups. Moreover, site-selective immersion was realized using a SAM having a pattern of hydrophilic and hydrophobic surfaces.<sup>31–32</sup> 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<sub>2</sub> was deposited and thin film was grown on the hydrophilic surface selectively. This technique can be used to fabricate any kind of micropattern so long as the film can be deposited from a solution. However, feature edge acuity must be improved if these patterns are to be applied to nano- and micro-sized devices.

In this study, we developed a novel method to realize SSD of thin films using a seed layer. We used a quartz crystal microbalance (QCM) to evaluate in detail the process by which anatase TiO<sub>2</sub> is deposited from an aqueous solution and found that nucleation and initial growth of it were accelerated on amorphous TiO<sub>2</sub> thin films compared with on octadecyl, phenyl, amino, or hydroxyl (silanol) groups. In our process, amorphous TiO<sub>2</sub> was shown to decrease the nucleation energy of anatase TiO<sub>2</sub> and provided nucleation sites for the formation of anatase TiO<sub>2</sub>. Amorphous TiO<sub>2</sub> thin film was deposited on silanol regions of patterned OTS-SAMs from TDD solution. This substrate was immersed in an aqueous solution containing Ti precursor to be used as a template for SSD. Anatase TiO<sub>2</sub> was selectively deposited on amorphous TiO<sub>2</sub> regions to form thin films, and thus a micropattern of anatase TiO<sub>2</sub> thin films was successfully fabricated.

## Experimental Section

**SAM Preparation.** The OTS-SAM was prepared by immersing the Si substrate in an anhydrous toluene solution containing 1 vol % OTS for 5 min under a N<sub>2</sub> atmosphere.<sup>10,14,16–17</sup> The OM-SAM, PM-SAM, and AET-SAM were prepared by immersing the Au-coated quartz crystal of a QCM (QCA917, Seiko EG&G Co., Ltd.) in a dicyclohexyl solution containing 1 vol % octadecylmercaptan (OM), phenylmercaptan (PM), or 2-aminoethanethiol (AET), respectively, for 30 min under a N<sub>2</sub> atmosphere.<sup>31–32</sup> Substrates with SAMs were then rinsed with anhydrous toluene to remove residual reagents. The OM-SAM, PM-SAM, and AET-SAM have octadecyl, phenyl, or amino groups, respectively. OTS-SAMs were exposed for 2 h to UV light (184.9 nm) through a mesh for transmission electron microscopy (TEM). The UV-irradiated regions became hydrophilic owing to the formation of Si–OH groups, while the nonirradiated part remained unchanged, that is, it was composed of hydrophobic octadecyl groups, which gave rise to a patterned OTS-SAM. This patterned SAM was used as a template for SSD of amorphous TiO<sub>2</sub> thin films. SAMs on quartz crystals of a QCM were exposed for 2 h to UV

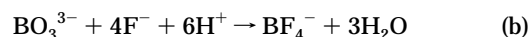
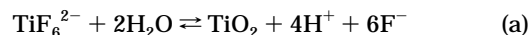


**Figure 1.** Deposition quantity of anatase TiO<sub>2</sub> on amorphous TiO<sub>2</sub>, octadecyl groups, phenyl groups, amino groups, or hydroxyl groups at (a) pH 1.5 or (b) pH 2.8 as a function of deposition time.

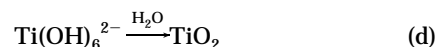
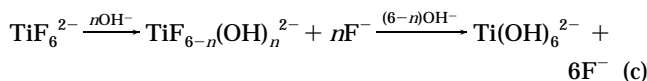
light without a photomask to assess the deposition rate of anatase TiO<sub>2</sub> on hydroxyl groups (OH) instead of on silanol groups (Si–OH). To check the successful formation of films and change of functional group, water drop contact angles were measured for irradiated and nonirradiated surfaces. The initially deposited OTS-SAM, OM-SAM, PM-SAM, and AET-SAM showed water contact angles of 96°, 96°, 76°, and 53°, respectively. UV-irradiated surfaces of SAMs (OH-SAM) were, however, wetted completely (contact angle < 5°).

**Hydrolysis of TDD and Formation of Amorphous TiO<sub>2</sub> Thin Films.** The 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 a N<sub>2</sub> atmosphere using a glovebox. All glassware was dried in a drybox at 50 °C before use. The estimated partial pressure of H<sub>2</sub>O in a N<sub>2</sub> atmosphere is below 0.1 hPa. Chlorine atoms of TDD react with H<sub>2</sub>O and change into OH groups, which further react with the silanol groups of the SAM resulting in the formation of Ti–O–Si bonds.<sup>33</sup> The ethoxy group, 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>33</sup> 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 the OTS-SAM but were not observed on octadecyl surfaces. A micropattern of amorphous TiO<sub>2</sub> thin films was thus fabricated on a patterned OTS-SAM. Additionally, the OM-SAM was formed on the Au-coated quartz crystal and then modified to a hydroxyl group surface (OH-SAM) by UV irradiation. A quartz crystal covered by hydroxyl groups was immersed in the TDD solution to form an amorphous TiO<sub>2</sub> thin film and was used for quantitative analysis by a QCM.

**Deposition of Anatase TiO<sub>2</sub> Thin Films.** Equal volumes (50 mL) of aqueous solutions of 0.10 M ammonium hexafluorotitanate ([NH<sub>4</sub>]<sub>2</sub>TiF<sub>6</sub>) and 0.30 M boric acid (H<sub>3</sub>BO<sub>3</sub>) were mixed with HCl (0.1 mL for pH 2.8, 0.6 mL for pH 1.5) to deposit anatase titanium dioxide at 50 °C.<sup>18</sup> Micropatterns of amorphous TiO<sub>2</sub> thin films fabricated on a patterned OTS-SAM or Au-coated quartz crystal of a QCM with SAMs were immersed in an aqueous solution upside down to avoid the deposition of TiO<sub>2</sub> particles by gravity (Figure 1). The deposition of anatase TiO<sub>2</sub> proceeds by the following mechanism:



Equation a is described in detail by the following two equations:



Fluorinated titanium complex ions gradually change into tita-

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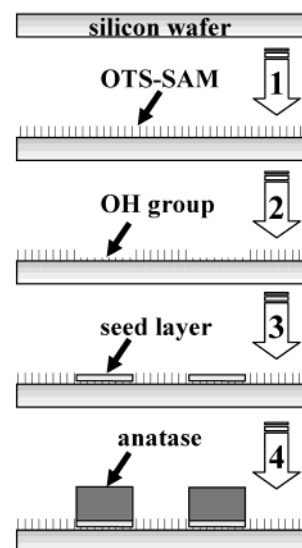


nium hydroxide complex ions in an aqueous solution as shown in eq c. Anatase  $\text{TiO}_2$  is formed from titanium hydroxide complex ions ( $\text{Ti}(\text{OH})_6^{2-}$ ) in eq d, and thus the supersaturation degree and the deposition rate of  $\text{TiO}_2$  depend on the concentration of titanium hydroxide complex ions. A high concentration of  $\text{H}^+$  displaces the equilibrium to the left in eq a, and a low concentration of  $\text{OH}^-$  by replacement with  $\text{F}^-$  ions suppresses ligand exchange in eq c and decreases the concentration of titanium hydroxide complex ions at a low pH such as pH 1.5. The solution actually remained clear at pH 1.5, showing its low degree of supersaturation. On the other hand, the solution at a high pH such as pH 2.8 became turbid because of the formation of homogeneously nucleated anatase  $\text{TiO}_2$  particles caused by the high degree of supersaturation. At pH 1.5, anatase  $\text{TiO}_2$  thin films formed by heterogeneous nucleation in the solution, while at pH 2.8 heterogeneous nucleation and deposition of particles occurred. The deposition behavior of anatase  $\text{TiO}_2$  onto amorphous  $\text{TiO}_2$  and onto different SAMs at two different pH values was evaluated by QCM.

## Results and Discussion

**Quantitative Analysis of the Deposition of Anatase  $\text{TiO}_2$  onto an Amorphous  $\text{TiO}_2$  Thin Film or onto SAMs.** Quartz crystals covered with amorphous  $\text{TiO}_2$  thin film, OM-SAM ( $\text{CH}_3$ ), PM-SAM (Ph), AET-SAM ( $\text{NH}_2$ ), or OH-SAM (OH) were immersed in a solution containing 0.05 M  $\text{TiF}_6^{2-}$  and 0.015 M  $\text{BO}_3^{3-}$  at pH 1.5 or pH 2.8 (Figure 1). The supersaturation degree of the solution at pH 1.5 was low as the high concentration of  $\text{H}^+$  suppressed  $\text{TiO}_2$  generation in eq a, and hence the deposition reaction progresses slowly with no homogeneous nucleation occurring in the solution. We found that anatase  $\text{TiO}_2$  was deposited on an amorphous  $\text{TiO}_2$  thin film faster than on OM-, PM-, AET-, or OH-SAMs at pH 1.5. This shows that the deposition of anatase  $\text{TiO}_2$  was accelerated on amorphous  $\text{TiO}_2$  compared with on silanol, amino, phenyl, or octadecyl groups. Amorphous  $\text{TiO}_2$  probably decreases the nucleation energy of anatase  $\text{TiO}_2$ . The difference in deposition rate enables SSD to be achieved. The amorphous  $\text{TiO}_2$  thin film can be used as a seed layer to accelerate the deposition of anatase  $\text{TiO}_2$ . The deposition rate at pH 2.8 was larger than that at pH 1.5 because of the high degree of supersaturation, and homogeneously nucleated particles in the solution deposited on the whole surface of the substrate, regardless of the surface functional groups. The thickness of anatase  $\text{TiO}_2$  thin film deposited on a quartz crystal covered with amorphous  $\text{TiO}_2$  at pH 1.5 for 1 h and at pH 2.8 for 30 min was estimated to be 36 and 76 nm, respectively, assuming the density of anatase type  $\text{TiO}_2$  to be 3.89 g/cm<sup>3</sup>.

**Patterning of the OTS-SAM and SSD of Amorphous  $\text{TiO}_2$ .** An OTS-SAM was prepared on a silicon substrate. The calculation was performed at the Hartree-Fock/3-21G(\*) level utilizing the Spartan program (Spartan '02 for Windows, Wavefunction, Inc.)<sup>34</sup> to optimize the geometry of the OTS molecule. The distance between the hydrogen atom at the end of the molecule and silicon was calculated to be 2.43 nm, and this will be the thickness of the OTS-SAM. The OTS-SAM was modified by UV irradiation to give rise to a micropattern with silanol/octadecyl groups (Figure 2) and was observed with a scanning electron microscope (SEM; S-3000N, Hitachi Ltd.). Silanol regions showed white contrast in SEM micrographs (Figure 3 (1-a), (1-b)) compared with non-UV-irradiated regions. In general, a high area shows as white compared with a low area. However, high areas such as OTS-SAM regions appeared black compared with low silanol regions. SEM contrast is affected by many

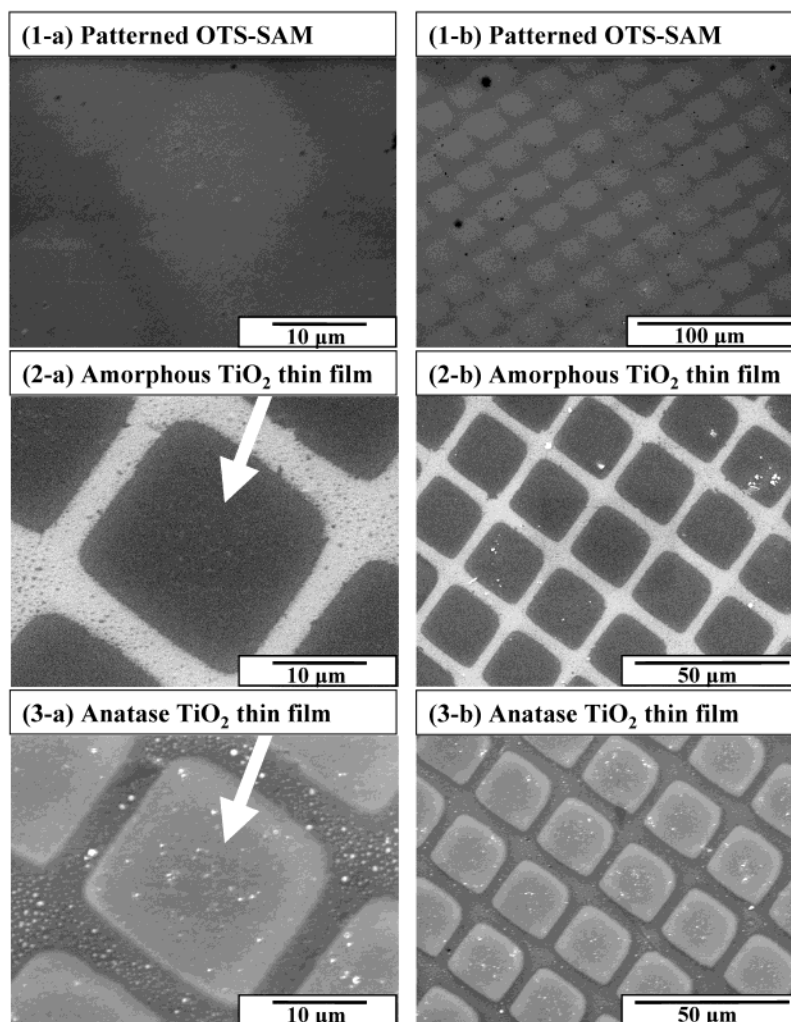


**Figure 2.** Schematic for SSD of anatase  $\text{TiO}_2$  thin films using a seed layer. Process sequence: 1, SAM preparation; 2, patterned UV irradiation; 3, site-selective amorphous  $\text{TiO}_2$  seed deposition on silanols; 4, site-selective anatase deposition on amorphous  $\text{TiO}_2$  seed regions.

factors. The amorphous  $\text{SiO}_2$  layer on the surface of a silicon wafer probably emits many secondary electrons compared with the OTS-SAM, and the OTS-SAM inhibits the emission of secondary electrons from under the amorphous  $\text{SiO}_2$  layer. Hence, the regions covered by the OTS-SAM appeared black compared with silanol group regions. This phenomenon was also observed with patterned PTCS-SAMs and APTS-SAMs.<sup>23</sup> The patterned SAM was further immersed in the solution containing TDD molecules for 30 min.<sup>21</sup> Amorphous  $\text{TiO}_2$  was selectively deposited on silanol regions and showed black contrast in SEM micrographs (Figure 3 (2-a), (2-b)) compared with non-UV-irradiated regions.<sup>21</sup> Amorphous  $\text{TiO}_2$  deposited from our solution probably emits fewer secondary electrons compared with the amorphous  $\text{SiO}_2$  layer on the surface of a silicon wafer, and the  $\text{TiO}_2$  layer would inhibit the emission of secondary electrons from under the amorphous  $\text{SiO}_2$  layer. This probably causes the contrast in Figure 3 (2-a), (2-b). The line edge roughness was estimated in the same manner as we used for titanium dioxide films.<sup>18,21</sup> Line width measurements at 15 equally spaced points on each line indicate an average printed line width of 23.3  $\mu\text{m}$ . Line edge roughness, as measured by the standard deviation of the line width, is  $\sim 0.5 \mu\text{m}$ . This represents an  $\sim 2.1\%$  variation (i.e., 0.5/23.2) in the nominal line width. X-ray diffraction (XRD) measurements (Rigaku RU-200) with  $\text{Cu K}\alpha$  radiation (40 kV, 30 mA) for as-deposited thin films showed that they were composed of amorphous phases.<sup>21</sup> The ratio of oxygen to titanium was evaluated after 20 min of  $\text{Ar}^+$  ion sputtering to avoid the influence of the contaminated layer on the surface.<sup>21</sup> The 1s peak of O can be deconvoluted into two curves (the 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 ( $\text{Ti}/\text{O}/\text{Cl}/\text{C} = 1:2.2:0.17:0.37$ ).<sup>21</sup>

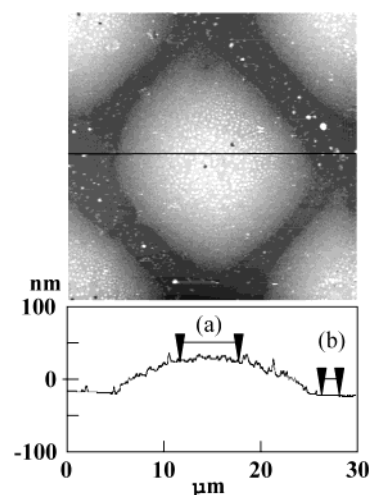
**SSD of Anatase  $\text{TiO}_2$  on a Seed Layer.** A micropattern having amorphous  $\text{TiO}_2$  and octadecyl groups was immersed in an aqueous solution at pH 1.5 for 1 h (Figure 2). Deposited thin films made it appear white compared with octadecyl group regions in SEM micrographs (Figure 3 (3-a), (3-b)) because of the difference in height. The

(34) Hehre, W. J. *Spartan '02 for Windows*; Wavefunction, Inc.: Irvine, CA.



**Figure 3.** SEM micrographs of [(1-a), (1-b)] a patterned OTS-SAM, [(2-a), (2-b)] a micropattern of amorphous  $\text{TiO}_2$  thin films, and [(3-a), (3-b)] a micropattern of anatase  $\text{TiO}_2$  thin films deposited at pH 1.5.

feature edge acuity of the anatase  $\text{TiO}_2$  pattern was  $\sim 2.1\%$  variation (i.e.,  $0.5/23.2$ ) and was much the same as we calculated from the amorphous  $\text{TiO}_2$  pattern. This resemblance was observed from Figures 2a and 3a. These micrographs were taken from the same position. Variations of these patterns were much better than that of the pattern fabricated with a lift-off process<sup>18</sup> and the usual 5% variation afforded by current electronics design rules. Additionally, these variations were similar to that of a TEM mesh (2.1%) we used for Figure 3. Therefore, variations of these patterns can be improved through the use of a high-resolution photomask. Site-selective deposition was also possible for the 2 or 3 h reaction. However,  $\text{TiO}_2$  began to deposit on OTS regions gradually after 4 h of soaking. Homogeneously nucleated particles were deposited on the whole area of the substrate (Figure 3a), but these particles can be removed easily by ultrasonication. The thin films were evaluated by an X-ray diffractometer (RAD-C, Rigaku) with Cu K $\alpha$  radiation (40 kV, 30 mA) and a Ni filter plus a graphite monochromator. Deposited films showed weak XRD patterns of anatase type  $\text{TiO}_2$  because the films were not sufficiently thick to show strong diffraction. This finding provides evidence for the deposition of anatase  $\text{TiO}_2$  on amorphous  $\text{TiO}_2$  regions. An atomic force microscope (AFM; Nanoscope E, Digital Instruments) image showed anatase  $\text{TiO}_2$  thin films to be higher than octadecyl group regions (Figure 4). The center of the anatase  $\text{TiO}_2$  thin film region was 61



**Figure 4.** AFM image, cross-section profile, and (a), (b) measurement areas of surface roughness of a micropattern of anatase  $\text{TiO}_2$  thin films deposited at pH 1.5.

nm higher than the octadecyl regions, and the thickness of the anatase  $\text{TiO}_2$  thin film was estimated to be 36 nm considering the thickness of the amorphous  $\text{TiO}_2$  thin film (27 nm)<sup>23</sup> and OTS molecules (2.4 nm) (Figure 2). This result is similar to that estimated by QCM measurement (36 nm). The surface roughness (root mean square, rms)

of the anatase TiO<sub>2</sub> thin film was estimated using an AFM image and the equation

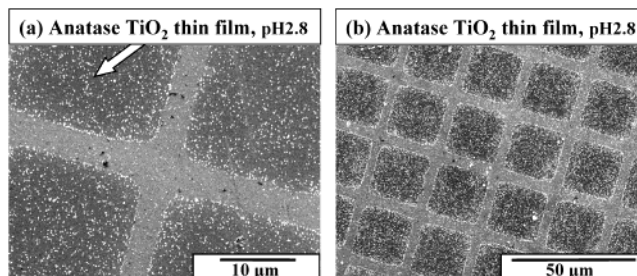
$$\text{rms (standard deviation)} = [\sum_i (Z_i - Z_{\text{ave}})^2 / n]^{1/2} \quad (\text{e})$$

$Z_i$  is the height at point  $i$ ,  $Z_{\text{ave}}$  is the average of  $Z$  (height), and  $n$  is the number of data points.

The AFM image showed the film roughness to be 3.7 nm (horizontal distance between measurement points of 6.0  $\mu\text{m}$ ) (Figure 4 (a)), which is less than that of the amorphous TiO<sub>2</sub> thin film (rms 9.7 nm, 27 nm thick, horizontal distance between measurement points of 6.0  $\mu\text{m}$ ).<sup>23</sup> Additionally, the roughness of the octadecyl group regions was shown to be 0.63 nm (horizontal distance between measurement points of 1.8  $\mu\text{m}$ ) (Figure 4 (b)).

Amorphous TiO<sub>2</sub> accelerated the deposition of anatase TiO<sub>2</sub> and showed its excellent performance as a seed layer. The feature edge acuity of anatase TiO<sub>2</sub> patterns was estimated to be approximately 2.1% using the same method as used for a micropattern fabricated by the lift-off process<sup>18</sup> and was the same as that of amorphous TiO<sub>2</sub>.<sup>21</sup> The feature edge acuity could be improved by using a higher feature edge acuity photomask since this variance is similar to that of the TEM mesh (2.1%). XRD measurements for the thin film deposited for 1 h did not show any peaks since the deposited quantity was not sufficient to show any diffraction; however, the thin film deposited for 7 h was composed of anatase TiO<sub>2</sub>. Anatase TiO<sub>2</sub> thin films were not peeled off by sonication in ethanol for 10 min and showed strong adhesion to the amorphous TiO<sub>2</sub> layer. This suggests that strong chemical bonds were formed between anatase TiO<sub>2</sub> and amorphous TiO<sub>2</sub>.

**Deposition of Anatase TiO<sub>2</sub> in an Aqueous Solution at pH 2.8.** A micropattern which had amorphous TiO<sub>2</sub> and octadecyl groups was immersed in an aqueous solution at pH 2.8 for 30 min. Many particles were observed over the whole area of the substrate (Figure 5) and were formed in the solution homogeneously because of the high degree of supersaturation. These observations are consistent with the results of QCM analysis. XRD measurements for the precipitates deposited for 30 min did not show any peaks since the deposited quantity was not



**Figure 5.** SEM micrographs of a micropattern of anatase TiO<sub>2</sub> thin films deposited at pH 2.8.

sufficient to show any diffraction. However, the precipitates deposited for 4 h were composed of anatase TiO<sub>2</sub>. Anatase TiO<sub>2</sub>, which has a large surface area, was deposited from an aqueous solution at low temperature and may be suitable as a photonic catalyst.<sup>35</sup> However, SSD was not achieved at pH 2.8 because of the deposition of homogeneously nucleated particles, and the control of supersaturation was shown to be important for SSD.

## Conclusions

We have developed a novel method to realize SSD of thin films using a seed layer. The deposition of anatase TiO<sub>2</sub> from an aqueous solution was shown by QCM analysis to be accelerated on amorphous TiO<sub>2</sub> thin films compared with on octadecyl, phenyl, amino, or hydroxyl groups. A micropattern having amorphous TiO<sub>2</sub> regions and octadecyl regions to be used as a template was prepared and immersed in the aqueous solution. Anatase TiO<sub>2</sub> was successfully deposited on amorphous TiO<sub>2</sub> regions, and amorphous TiO<sub>2</sub> thin film was shown to act effectively as a seed layer to accelerate the nucleation and initial growth of anatase TiO<sub>2</sub>. Consequently, SSD was achieved and a micropattern of anatase TiO<sub>2</sub> was fabricated in the aqueous solution using a seed layer.

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