Templated Site-Selective Deposition of Titanium Dioxide on Self-Assembled Monolayers

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Received August 14, 2001. Revised Manuscript Received November 30, 2001

TiO_2 thin films were grown on several kinds of SAMs (self-assembled monolayers) using TC (titanium tetrachloride), TDD (titanium dichloride diethoxide), or TE (titanium tetraethoxide) as a starting material. We discussed the thin film formation mechanism and improvement of feature edge acuity through controlling the reactivity by changing functional groups of starting material and the surface functional groups of SAMs. The deposition of TiO_2 from TC or TDD solution was promoted in the silanol group, and the deposition was suppressed on OTS (octadecyltrichloro-silane) SAM. On the other hand, TE was deposited regardless of the type of surface functional group in the whole area of patterned SAMs. The silanol group, which has high hydrophilicity, accelerated the growth of TiO_2, and the OTS SAM, which has hydrophobicity, suppressed the growth of TiO_2. It is also clarified that the chlorine atom in the starting material has high reactivity with silanol groups of SAMs.

Introduction

Titanium dioxide (TiO_2) thin films are of interest for use in a range of applications including microelectronics,[1] optical cells,[2] solar energy conversion,[3] highly efficient catalysts,[4] microorganism photolysis,[5] antifogging and self-cleaning coatings,[6] gratings,[7] gate oxides in MOSFET (metal-oxide-semiconductor field effect transistor),[8,9] and so on. Accordingly, fabrication of thin films and micropatterns of TiO_2 by several methods has been attempted.

TiO_2 films were prepared from solutions by some methods.[10−17] Deki et al.[10] prepared anatase type TiO_2 thin films on glass substrates from $(NH_4)_2TiF_6$ aqueous solution with addition of H_3BO_3 as a F^- ion scavenger. The films were constructed of polycrystalline particles which are smaller than the wavelength of visible light. Therefore, transparent TiO_2 films were fabricated. In this method, anatase type TiO_2 films were prepared at low temperature (25 °C) from an aqueous solution. Rutile TiO_2 thin films (0.18 μm) were also prepared on α-Al_2O_3 substrates by hydrothermal treatment of a solution of a mixture of TiO_4^{4-} (0.5 M) and HNO_3 (2.0 M) at low temperatures (100−200 °C).[11] The film consisted of short columnar grains (50×20 nm^2) and is uniform, homogeneous, and without visible defects. Lin et al.[12] synthesized amorphous TiO_2 gel films on the SAM (self-assembled monolayer) of OTS (octadecyltrichloro-silane) using $Ti(OC_3H^i{}_7)_4$-derived TiO_2 sols. The OTS SAM induced precipitation of anatase phase at a rather low temperature of 200 °C and accelerated anatase-to-rutile phase transformation when a mole ratio of H_2O:$Ti(OC_3H^i{}_7)_4$ as low as 0.5 was employed for sol preparation. TiO_2 thin films were also deposited in aqueous HCl solutions of $TiCl_4$ for 2 h at 80 °C on SAMs of SO_3H groups which are formed on glass substrates.[13] $TiCl_4$ is hydrolyzed in an aqueous solution to form TiO_2 particles, and they adhered to a substrate. The films consisted of TiO_2 crystallites around 120 nm in size.

Micropatterning of TiO_2 was attempted by several methods referring to these thin film fabrication processes.[18−22] We fabricated micropatterns of anatase

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10.1021/cm0107528 CCC: $22.00 © 2002 American Chemical Society
Published on Web 02/20/2002

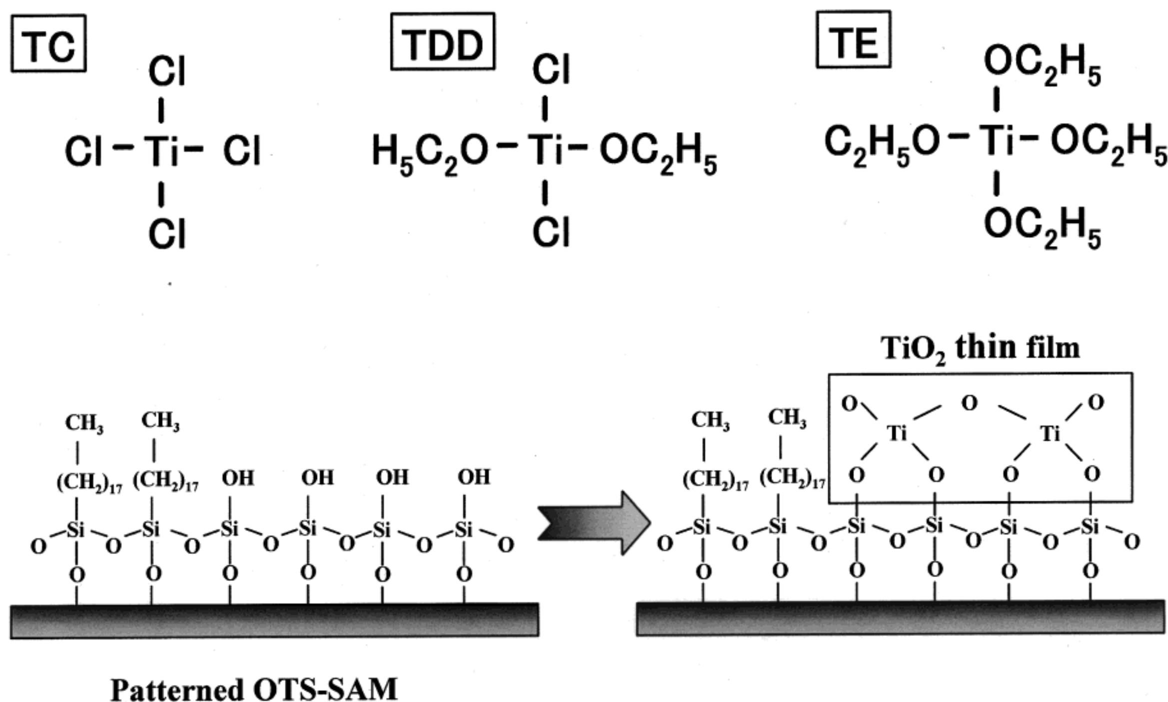

Figure 1. Conceptual process for selective deposition of titanium oxide thin films using self-assembled monolayers.

type TiO_2 thin films on a patterned SAM. A PTCS (phenyltrichlorosilane) SAM was irradiated by UV light through a photomask to form silanol/phenyl micropattern and was used as a template.[18] Anatase type TiO_2 thin films were deposited on the whole area of a patterned SAM from $(NH_4)_2TiF_6$ aqueous solution with addition of H_3BO_3 at 50 °C for 6 h. Thin films on phenyl regions were then peeled off by sonication. Thin films on silanol region showed strong adhesion to silanol groups compared with those on phenyl regions. Consequently, a micropattern of anatase TiO_2 was fabricated at low temperature. However, the lift-off process causes a deterioration of feature edge acuity of a micropattern. Patterned thin films of TiO_2 were also deposited from aqueous solution of 0.5 M $TiCl_4$ in 6 M HCl at 80 °C for 2 h.[19] Regions of the SAM containing sulfonate surface functionality were created by the photooxidation (UV light 254 nm) of initially deposited thioacetate groups through a mask. During aqueous deposition of TiO_2 onto such engineered substrates, nanocrystalline anatase TiO_2 particles were deposited on the sulfonate regions of the monolayer. TiO_2 particles were selectively deposited and micropattern was fabricated at low temperature. However, the thin film consisted of particles that were nucleated and grown in the solution. It lowers the uniformity of the film. Tremel and co-workers[20] have described the micropattern of TiO_2. The gold-coated glass slides have been patterned by stamping using SAM of hexadecane thiols. Through the use of a thiol terminated with a styrene monomer, micropatterns (polystyrene/hexadecane) have been formed on the surface by graft polymerization of styrene. These patterned gold slides have then been used to template for the precipitation of TiO_2 from ethanolic solutions of $Ti[OCH(CH_3)_2]$ (titanium isopropoxide) with additional water vapor. TiO_2 was precipitated all over the template after immersing at room temperature for 10 h. After the cleavage of the polymer, TiO_2 over polystyrene was removed, and the patterned TiO_2 with the feature edge acuity being better than 1 μm was thus obtained. However, deposited TiO_2 film has many cracks and many TiO_2 particles on it. Additionally, improvement of feature edge acuity is necessary to enable the application of these patterns to electrical or optical devices.

We recently reported selective deposition of TiO_2 thin films[21,22] using TDD (titanium dichloride diethoxide) on a patterned SAM (self-assembled monolayer)[18,23–25] of OTS. TiO_2 was selectively deposited on silanol regions from TDD solution[21] or TDD vapor,[22] and micropatterns of TiO_2 were successfully fabricated. These patterns showed an ~2.1% variation in the nominal line width (23.2 μm), and cracks or TiO_2 particles were not observed on films. In these experiments, a patterned OTS SAM showed high selectivity as a template for selective growth, and TDD showed high ability for making uniform thin films on silanol regions selectively. However, higher resolution patterns are needed in applications such as microdevices, and mechanism of selective growth was not clarified yet.

Here, we evaluate several kinds of SAMs as templates for selective growth of TiO_2 and use several titanium compounds as starting materials (Figure 1). We discuss the mechanism of site-selective growth of TiO_2 and the conditions to fabricate high feature edge acuity patterns.

Experimental Section

SAM Preparation. An OTS SAM and a PTCS (phenyltrichlorosilane) SAM were prepared by immersion of the Si substrate (p-type Si (100)) in an anhydrous toluene solution containing 1 vol % OTS or PTCS, respectively, for 5 min under

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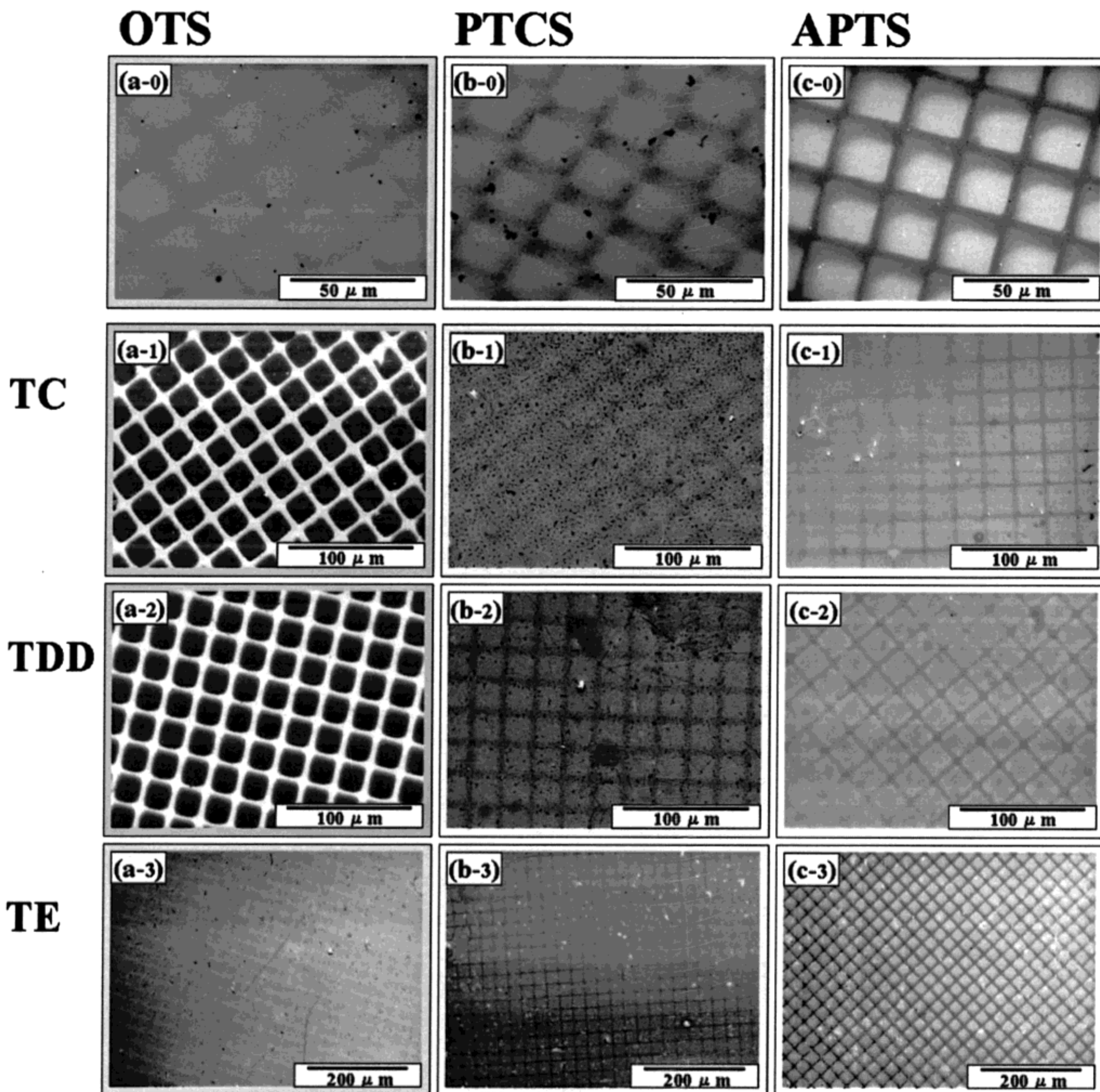

Figure 2. SEM photographs of OTS SAMs patterned by UV irradiation before (a-0) and after immersing in a TC solution (a-1), a TDD solution (a-2), or a TE solution (a-3), PTCS SAMs patterned by UV irradiation before (b-0) and after immersing in a TC solution (b-1), a TDD solution (b-2), or a TE solution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

a N_2 atmosphere.[18,21–25] APTS (3-aminoproyltriethoxysilane) SAM was prepared by immersion 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. The SAMs were exposed for 2 h to UV light (184.9 nm) (NL-UV253, Nippon Laser & Electronics Laboratory) 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 nonirradiated part remained unchanged. The OTS SAM has a methyl group at the end of a long methylene chain, and the PTCS SAM and the APTS SAM have a phenyl group and an amino group, respectively. The initially deposited OTS SAM, PTCS SAM, and APTS SAM showed water contact angles of 96, 74, and 48° measured by a sessile drop method, respectively. UV-irradiated surfaces of SAMs were, however, wetted completely (contact angle $< 5°$). Patterned SAMs were observed with a scanning electron microscope (SEM; S-3000N, Hitachi Ltd.), and silanol regions showed white contrast in SEM photographs (Figure 2: (a-0), (b-0), and (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 a vacuum, for the surface of silicon substrate covered with silanol groups, phenyl groups (PTCS) ,and amino groups (APTS) are −38.23, +0.63, and +22.0 mV,[26] respectively. The positively charged surface shows black contrast and the negatively charged surface shows white contrast in a SEM photograph.

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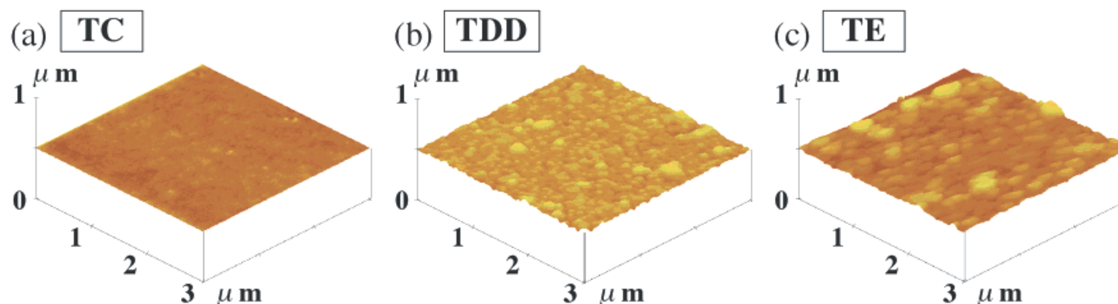

Figure 3. AFM images of thin films deposited from TC (a), TDD (b), or TE (c).

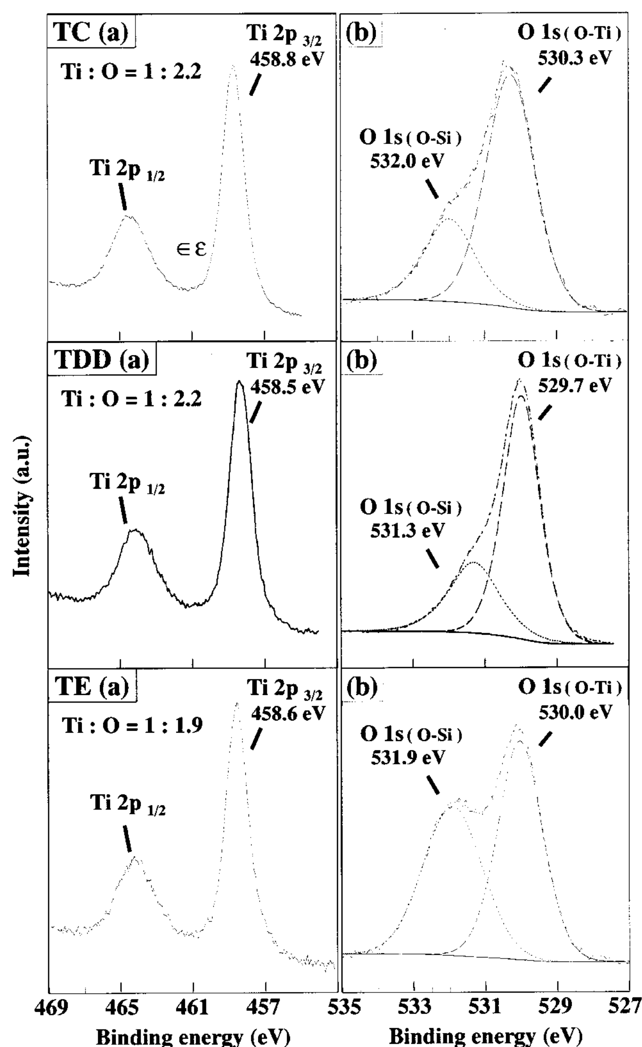

Figure 4. XPS spectra of (a) Ti 2p and (b) O 1s for titanium oxide thin films deposited from TC, TDD, or TE.

Formation of TiO_2 Thin Films. Patterned SAMs (OTS, PTCS, and APTS) were immersed into an anhydrous toluene (99.8%, water < 0.002%, Aldrich) solution containing 0.1 M TC for 3 min, 0.1 M TDD for 30 min, or 0.1 M TE for 3 h and 30 min (Figure 1). These experiments were carried out at room temperature under a N_2 atmosphere (99.99%, water < 550 ppb). Titanium compounds (TC, TDD, or TE) react with silanol groups of the SAM and H_2O molecules which are adsorbed on SAMs and/or remain in the solution. TiO_2 was then formed by the hydrolysis and condensation of titanium compounds (TC, TDD, or TE). TiO_2 was deposited on the whole area of large silanol surfaces (each being 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 (Mg Kα, 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 Cu Kα radiation (40 kV, 30 mA), 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.

Results and Discussion

Site-Selective Deposition of TiO_2 Thin Films. After having been immersed in the solution, the patterned SAMs were observed with a SEM. Selective deposition of TiO_2 was accomplished by a combination of TC and patterned OTS SAM and a combination of TDD and patterned OTS SAM (Figure 2: (a-1) and (a-2)). Thin films of TiO_2 were formed in silanol regions, and the deposition of TiO_2 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 (Figure 2: (b-1), (b-2), (c-1), and (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 (Figure 2: (a-3), (b-3), and (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. The 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], and 0.14 nm/min [TE]).

Thin films on phenyl groups (PTCS) or amino groups (APTS) deposited from TC or TDD were peeled off by sonication in acetone because these thin films do not have strong chemical bonds with SAMs. The micropattern of TiO_2 thin film was thus fabricated by sonication of TiO_2 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_2O molecules adsorbed on silanol groups compared with ethoxy groups. Accordingly, TiO_2 thin films are formed from TC and TDD in silanol regions through their hydrolysis with H_2O molecules

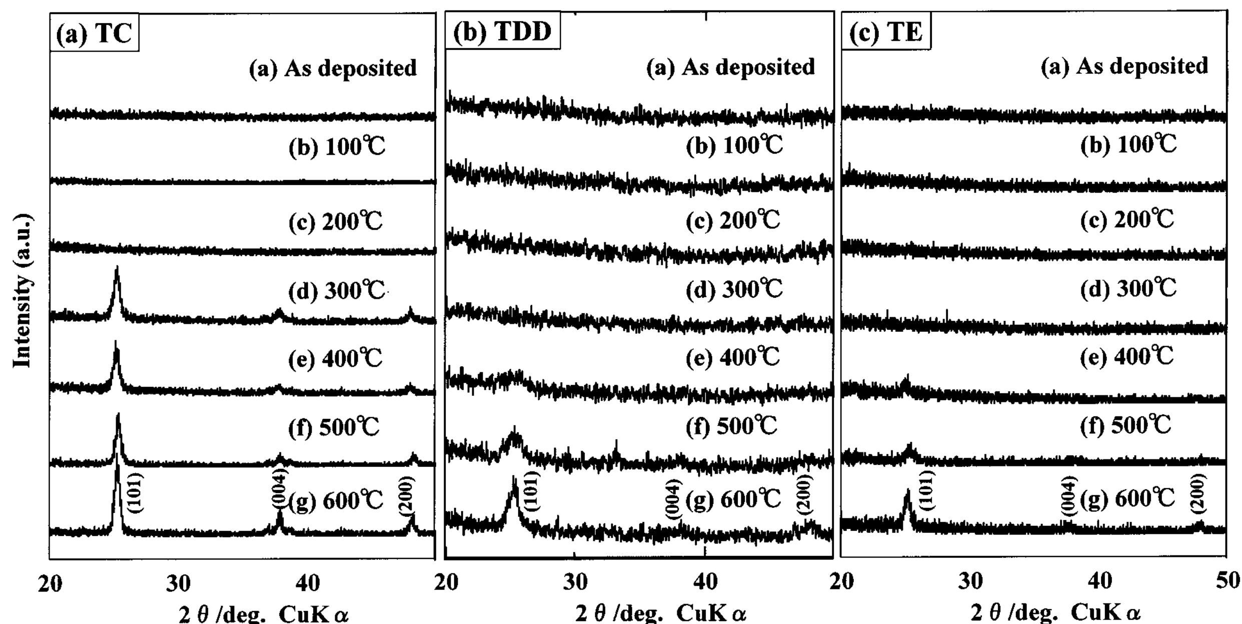

Figure 5. XRD patterns of thin films deposited from (a) TC, (b) TDD, or (c) TE changing with change in annealing temperature.

adsorbed on silanol groups. Thin films are formed in a short time before TC or TDD react with H_2O molecules in the solution to form TiO_2 particles. In contrast, TE molecules which have no chlorine atoms cannot easily react with H_2O molecules adsorbed on silanol groups, but they are hydrolyzed and condense with H_2O molecules in the solution to form TiO_2 particles. TiO_2 particles generated in the solution are then adsorbed on the whole area of patterned SAMs. These observations show that 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_2 from TC or TDD was sufficiently suppressed by OTS SAM, it was not suppressed well in the case of PTCS SAM or APTS SAM. The 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.[27−28] The water molecule is indispensable for the generation of TiO_2, 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_2 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. The OTS SAM could block any underlying silanols present from reacting with the solution titanium precursors, inhibiting nonselective TiO_2 deposition. Likewise, strong association of water at amino groups of APTS SAM can provide locally high levels of water required to form TiO_2 from the solution titanium precursors at these sites, leading to more nonselective deposition of TiO_2 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.[29] More recently, it has been observed that aromatic SAMs chemisorbed from aromatic solvent[30,31] form low-density SAMs having nanocavities capable of binding adsorbates from solution. The access of titanium precursor to free silanol groups at defect/cavity sites in such aromatic PTCS SAMs would be one of the reasons for film formation in the 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

$$\mathrm{RMS(standard\ deviation)} = [\sum_{i} (Z_i - Z_{ave})^2/n]^{1/2} \quad (1)$$

where Z_i is the height at point "i" (nm), Z_{ave} is the average of Z (height) (nm), and n is the number of data points.

The thin film deposited from TC onto silanol regions was the smoothest (roughness RMS: 2.6 [TC], 9.7 [TDD], and 14.0 [TE]), as shown in Figure 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 the TE molecule which has no chlorine atoms, and many particles which are generated in the solution are 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.

The line edge roughness of these patterns was estimated via the same way used for titanium dioxide films

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fabricated by a liquid-phase deposition process.[18] 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 μm. Line edge roughness, as gauged by the standard deviation of the line width, was ~0.5 μm, which represents a ~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,[18] 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 Figure 2, the feature edge acuity of a titanium dioxide pattern can be improved through the use of a higher feature edge acuity photomask. The TC molecule also has high selectivity to surface groups; thus, the feature edge acuity of the pattern was similar to that of the 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 for each of them was the same as that of the photomask.

Characterization of Deposited TiO_2 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],[21] and 458.6 eV [TE]) were seen from deposited thin films (Figure 4a). 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_2O_3 (456.7 eV) but is similar to that of TiO_2 (458.4−458.7 eV),[32−33] which suggests that titanium atoms in thin films are positively charged by the formation of direct bonds with oxygen.

The O 1s peak seen from the phase deposited on the silanol surface can be separated into two peaks (Figure 4b). Binding energy centered at about 532 eV is similar to that of SiO_2 and significantly decreased by Ar sputtering. These peaks are assigned to the natural oxide layer of silicon wafer and contamination on the surface. Binding energy centered at about 530 eV corresponds to that of TiO_2 (530.1 eV,[32] 529.9 eV[33]). 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, and 1/1.9/0.48/0 for TE. A trace of chlorine was detected in thin films deposited from TC or TDD but not in a thin film deposited from TE, since the 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.

X-ray diffraction measurements for as-deposited thin films from TC, TDD, or TE revealed that they were composed of amorphous phases (Figure 5). Heat treatment of the TiO_2 deposited from TC showed that the amorphous phase converts into a crystalline anatase phase above ~300 °C. On the other hand, amorphous TiO_2 deposited from TDD or TE converts into crystalline anatase above ~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 SiO_2 were also observed after annealing at 1000 °C, possibly due to the oxidation of the Si substrate itself.

Conclusions

TiO_2 thin films were grown on several kinds of SAMs using TDD, TC, or TE. The deposition of 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 surface functional group in the whole area of patterned SAMs. The silanol group which has high hydrophilicity accelerated the growth of TiO_2, and the OTS SAM which has hydrophobicity suppressed the growth of TiO_2. It is also clarified that the chlorine atom in the starting material has high reactivity with silanol groups of SAMs. The growth rate of thin film from TC was the fastest in our experiments, and these films showed a very smooth surface. This shows that growth rate and quality of thin films can be controlled by the selection of starting materials.

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