Selective Deposition and Micropatterning of Titanium Dioxide on Self-Assembled Monolayers from a Gas Phase

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Selective Deposition and Micropatterning of Titanium Dioxide on Self-Assembled Monolayers from a Gas Phase

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We present a novel process to gain selective deposition and generate high feature edge acuity micropatterns of TiO_2 thin films from a gas phase. Self-assembled monolayers (SAMs) of octadecyltrichloro-silane were modified to produce a methyl/silanol pattern and applied as templates to deposit TiO_2 through the use of titanium dichloride diethoxide. Patterned SAMs showed high selectivity for nucleation and growth of TiO_2, plus a feature edge acuity of the TiO_2 pattern well below 2.1%. Moreover, we developed a novel process to realize a two-dimensional arrangement of TiO_2 particles onto a SAM from a gas phase.

Introduction

Titanium dioxide has many useful electrical and optical properties, such as a high refractive index, high dielectrical permittivity, semiconductivity, excellent transmittance of visible light, and so forth, which make TiO_2 films useful in many fields: microelectronics,[1] optical cells,[2] solar energy conversion,[3] efficient catalysts,[4] microorganism photolysis,[5] antifogging and self-cleaning coatings,[6] gratings,[7–9] and so on. Novel ways to obtain micro/nano patterns of inorganic materials including titanium dioxide films were thoroughly investigated,[10–14] and we obtained micropatterned TiO_2 films on self-assembled monolayers (SAMs) of phenyltrichlorosilane (PTCS) via a liquid-phase deposition process with precipitation from aqueous solutions containing $TiF_6{}^{2-}$ ions.[10] The process called for PTCS SAM exposure to UV irradiation through a photomask to generate phenyl/silanol patterns and applying them as templates. TiO_2 (anatase) thin films were deposited on the entire SAM area. While thin films on the phenyl region easily peeled off by sonication, those on the silanol region did not, resulting in the formation of TiO_2 micropatterns, a process enabling the TiO_2 patterns to form on a large substrate minus heating. But TiO_2 was deposited on not only silanol regions but also the phenyl, making it necessary to deposit TiO_2 on silanol regions selectively to realize patterns of higher feature edge acuity applicable to micro/nano devices. Recently, we reported a high feature edge acuity pattern of TiO_2 thin films deposited on photopatterned SAMs using titanium dichloride diethoxide (TDD) solution.[14] TDD reacted with only silanol groups, and TiO_2 was deposited on silanol regions selectively. While the feature edge acuity of this pattern was well below 2.1% (line width 23.3 μm), a large number of TiO_2 particles generated by bulk nucleation formed in the TDD solution and their adhesion on TiO_2 thin films served to lower the feature edge acuity. Control of reaction conditions is essential to fabricate high-quality thin films.[15] We have developed a novel process to fabricate high feature edge acuity micropatterns of TiO_2 thin films from a gas phase.

Experimental Section

SAM Preparation. The octadecyltrichloro-silane (OTS) SAM was prepared by immersing the Si substrate in an anhydrous toluene solution containing 1 vol % OTS for 5 min under a N_2 atmosphere.[10,14,16,17] 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 Si–OH group formation, while the nonirradiated part remained unchanged, that is, it was composed of hydrophobic octadecyl groups, which gave rise to patterned OTS SAMs. To check successful film formation and functional group change, water drop contact angles were measured for irradiated and nonirradiated surfaces. Initially deposited OTS SAMs had a water contact angle of 96°, while the UV-irradiated SAM surface was saturated (contact angle <5°).

Hydrolysis of TDD and Formation of TiO_2 Thin Films. Patterned SAM substrates of OTS and an anhydrous toluene solution containing 0.1 M TDD were placed in an airtight Pyrex container in both air and N_2 atmospheres and kept at 90 °C for 2 h (Figure 1), the temperature selected for optimal TDD evaporation. TDD molecules evaporated and diffused to a patterned OTS SAM surface. TDD chlorine atoms react as H_2O transmutes to OH and further react with silanol groups of SAM, resulting in the formation of Ti–O–Si bonds.[18] Ti–O–Ti bonds are formed by chlorine hydrolysis; in addition, a film grows. To control supersaturation by partial H_2O pressure revision, experiments were conducted in air and N_2 atmospheres. Esti-

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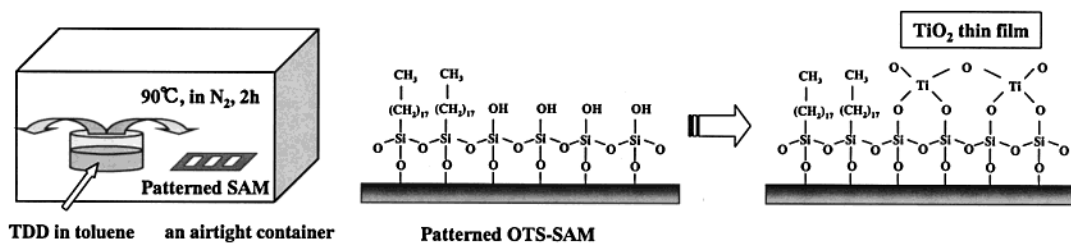(18) Lee, L. H. *J. Colloid Interface Sci.* **1968**, *27*, 751.

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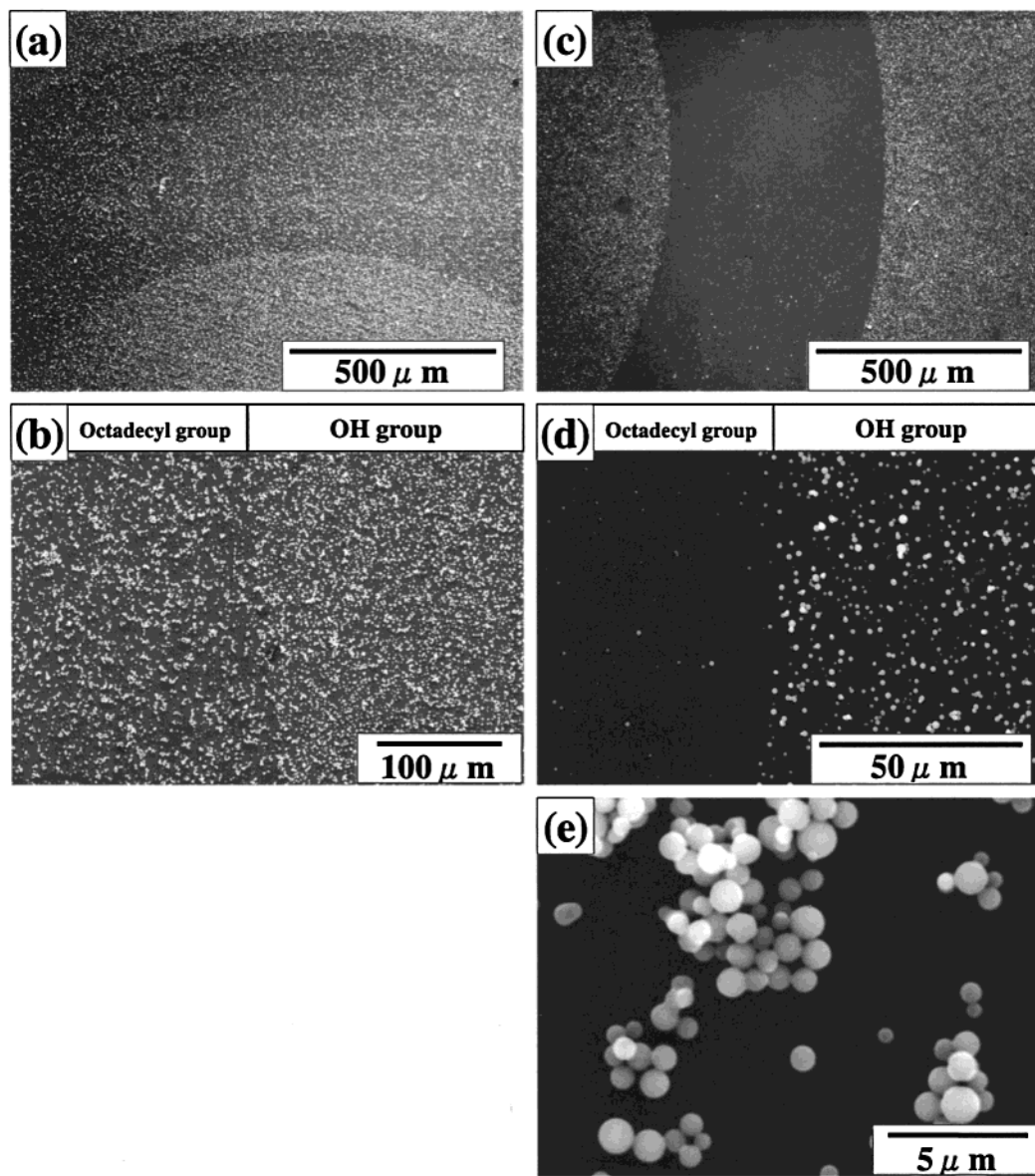

Figure 2. SEM photographs of TiO₂ particles (a and b) before and (c and d) after sonication and (e) magnified TiO₂ particles.

mated partial H_2O pressure in air and N_2 atmospheres was 14.0 hPa and below 0.1 hPa, respectively.

Results and Discussion

Micropatterning of TiO₂ Particles. Patterned SAM substrates of OTS and an anhydrous toluene solution containing 0.1 M TDD were placed separately in an airtight container in the air and kept at 90 °C for 2 h. A scanning electron microscope (SEM; S-3000N, Hitachi, Ltd.) revealed many spherical particles on the whole surface of a patterned OTS SAM after reaction (Figure 2a,b), a significant number of which aggregated (Figure 2e). 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 was determined to be 16% and 10%, respectively.

Supersaturation in the experiment in air was higher than that in an N_2 atmosphere. It is considered that very thin TiO₂ films and/or particles were generated on silanol groups, with small TiO₂ particles generated in the air first. Minute particles, like clusters of initial nuclei, formed in oxygen are transferred to a silanol surface by convection
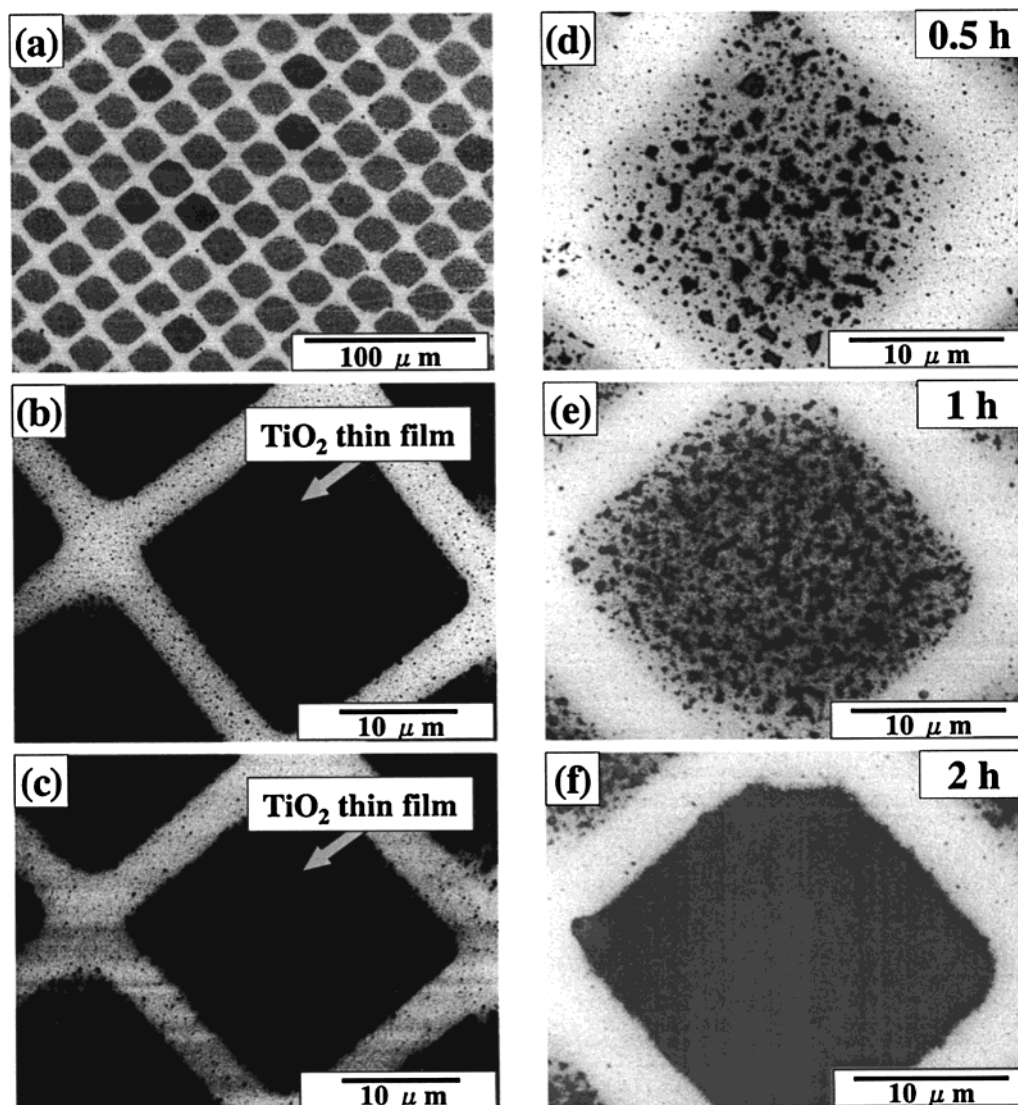
Figure 3. SEM photographs of (a) a micropattern of as-deposited thin films (2 h), (b) magnified area of (a), (c) after annealing of (b) at 600 °C for 3 h, and thin films deposited for (d) 0.5 h, (e) 1 h, and (f) 2 h.

and gravity and react with H_2O 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 H_2O between the silanol and octadecyl regions.

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 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 (Figure 2c,d). Consequently, a two-dimensional selective arrangement of TiO_2 particles resulted.

Sonication treatment revealed that the TiO_2 particles stick much more firmly to the silanol surface than to the octadecyl, implying that bonding between the nucleating (TiO_2) phase and the silanol surface is far stronger than that occurring on its octadecyl counterpart.

Selective deposition of TiO_2 particles due to their strong bond with silanol group surfaces is much like the selective deposition of SiO_2 particles on silanol surfaces as reported recently.[16,17] 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 TiO_2 Thin Films. Patterned OTS SAMs and a TDD solution were placed in an airtight container in an 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 (Figure 3a,b). Accordingly, a micropattern of 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
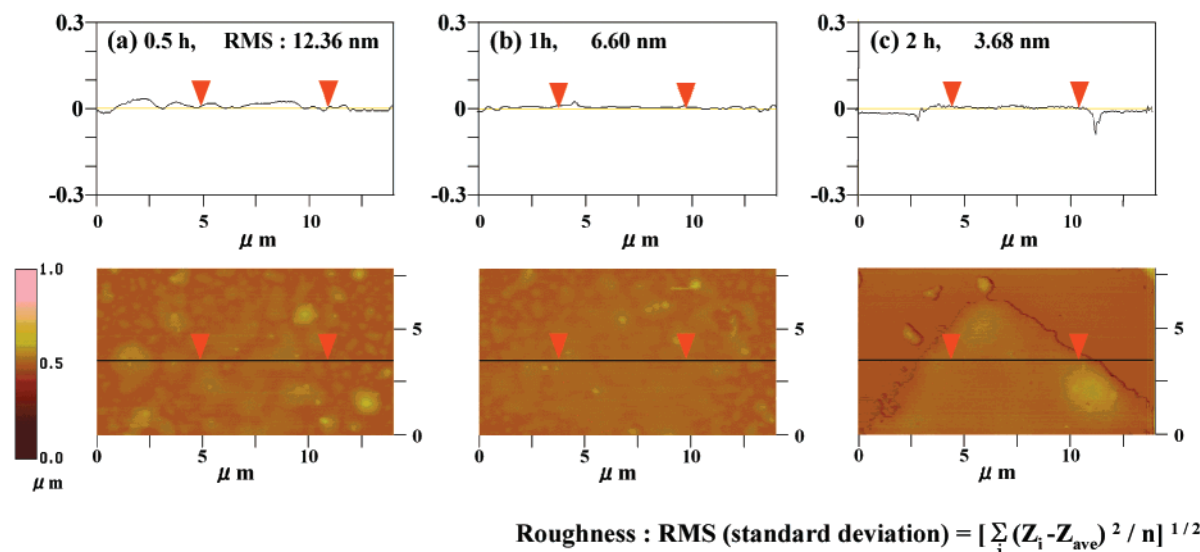
$$\text{Roughness : RMS (standard deviation)} = \left[\sum_i (Z_i - Z_{ave})^2 / n \right]^{1/2}$$

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

nucleation and TiO$_2$ growth of thin films as observed by SEM (Figure 3d–f). Many islands of deposited 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 TiO$_2$ particles generated by bulk nucleation were observed on TiO$_2$ thin films deposited from TDD liquid solution,[14] but none were detected by SEM on the thin films deposited from a gas phase in an 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.[10] Line width measurements at 15 equally spaced points on each line (Figure 3b) 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,[10] exceeds the usual 5% variation afforded by current electronics design rules, and very nearly equals that of the pattern deposited from a TDD solution.[14] Since this variance is similar to that of the TEM mesh (2.1%) we used for Figure 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 root mean square (rms) can be expressed as

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

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

Many islands were seen at the start of film formation (Figure 4a). 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 2 h of reaction were about 20 nm thick. The average growth rate (10 nm/h) more or less equals one-sixth of that for the liquid solution process (~60 nm/h).[14]

Characterization of Deposited TiO$_2$ Thin Films. TiO$_2$ 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 (Mg Kα, 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 (Figure 5a). 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$_2$O$_3$ (456.7 eV) but is less than that of TiO$_2$ (458.4–458.7 eV),[14,19,20] 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) (Figure 5b). The binding energy of the film is like that of TiO$_2$ (530.1 eV,[14,19] 529.9 eV[20]). 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$_2$ 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 of sputtering.

TiO$_2$ thin films on UV-irradiated OTS SAMs were assessed by a Fourier transform infrared spectrometer (FT-IR 610, Jasco, Ltd.), with a UV-irradiated OTS SAM used as a reference. The absorption band at 948.8 cm^{-1} appearing in the spectrum can be assigned to Ti–O–Si (950 cm^{-1}),[21] indicating that TDD chlorine atoms react with H$_2$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 Cu Kα radiation (40 kV, 30 mA) for as-deposited particles and thin films revealed them to be composed of amorphous

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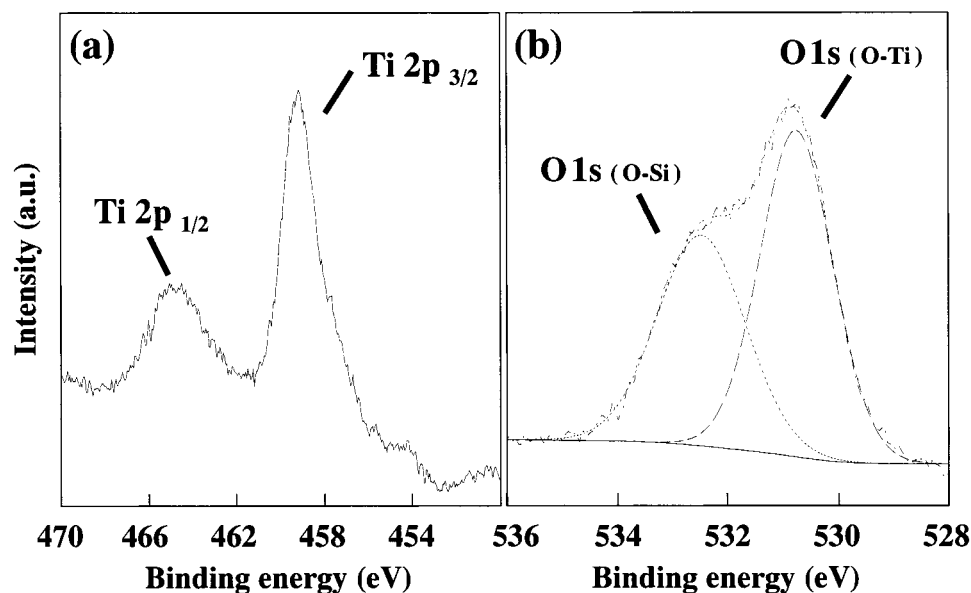
Figure 5. XPS spectra of (a) Ti 2p and (b) O 1s for titanium oxide thin films formed on the silanol region of OTS SAMs.

phases. Heat treatment of the TiO_2 showed that the amorphous phase converts into the crystalline anatase phase above ~400 °C and its crystallinity improves with a higher annealing temperature. The anatase phase further transforms 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 from oxidation of the Si substrate itself.

After annealing the micropattern of titanium dioxide shown in Figure 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 (Figure 3c). These results suggest that high feature edge acuity micropatterns of anatase-type TiO_2 can also be formed by our new patterning and heat treatment process.

Conclusions

TiO_2 thin films were selectively deposited on silanol areas of SAM in an N_2 atmosphere from the gas phase. Patterned SAMs showed high selectivity for nucleation and TiO_2 growth; hence, feature edge acuity of the TiO_2 pattern matched that of a photomask and equals that of the pattern formed in a TDD solution.[14] TiO_2 particles generated by bulk nucleation were observed in a TDD solution,[14] 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.