Atomic Layer Deposition of Titanium Oxide on Self-Assembled-Monolayer-Coated Gold

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We demonstrate an atomic layer deposition of TiO_2 thin films on self-assembled monolayers of ω-functionalized alkanethiolates. The TiO_2 thin films were grown on OH-terminated alkanethiolate monolayer-coated gold by atomic layer deposition at 100 °C. The atomic layer deposition of the TiO_2 thin films is self-controlled and extremely linear relative to the number of cycles. Selective deposition of the TiO_2 thin film using atomic layer deposition was accomplished with patterned self-assembled monolayers as templates. Microcontact printing was done to prepare the patterned monolayers of the alkanethiolates on gold substrates. The selective atomic layer deposition is based on the fact that the TiO_2 thin film is selectively deposited only on the regions exposing OH-terminated alkanethiolate monolayers of the gold substrates, because the regions covered with CH_3-terminated monolayers do not have any functional group to react with precursors.

Introduction

Self-assembled monolayers (SAMs) of ω-functionalized alkanethiolates on gold have enormous application prospects, because the surface properties are determined by the chemical nature of the terminal group of the alkanethiols.[1,2] Potential applications include thin film deposition, high-resolution patterning,[3,4] biomolecule immobilization,[5,6] molecular electronics,[7,8] and chemical sensing.[9,10] Recently, thin film deposition on alkanethiolate SAM-coated gold has been investigated in a number of publications.[11−13] To successfully deposit thin films on alkanethiolate SAM-coated gold, it is necessary for the SAMs to withstand the temperatures used in film formations. Since the alkanethiolate SAMs on gold can withstand air (or vacuum) temperatures only as high as 150 °C,[14] a critical requirement for the use of the deposition method with alkanethiolate SAM-coated gold as substrate is the temperature to deposit thin films. Atomic layer deposition (ALD) is a gas-phase thin film deposition method working at low temperatures. During the past decade, ALD has attracted considerable attention as a method for manufacturing high-quality thin films and producing tailored molecular structures.[15−17] Since the ALD is a low-temperature process, it can be applied to thin film deposition on alkanethiolate SAM-coated gold.

Among various patterning methods, there has been a growing interest in forming a patterned thin film by site-selective deposition on a patterned monolayer as a simple low-cost fabrication process.[12,18] Patterned alkanethiolate SAMs have been used as molecular resists at the surface for selective deposition of thin films.[12] Selective depositions of thin films using chemical vapor deposition, electroplating, and electroless deposition have been also accomplished with patterned SAMs as templates.[12] The ALD method relies on sequential saturated surface reactions which result in the formation of a monolayer in each sequence. The successive self-terminating growth mechanism in ALD inherently eliminates gas-phase reactions. Elimination of the gas-phase reaction results in emphasizing the importance of the surface reaction. The ALD process offers an ideal method for selective deposition of thin films on patterned SAMs, because it is very sensitive to the surface conditions of the substrates.

Thin films of titanium dioxide (TiO_2) have high refractive index, excellent transmittance in the visible

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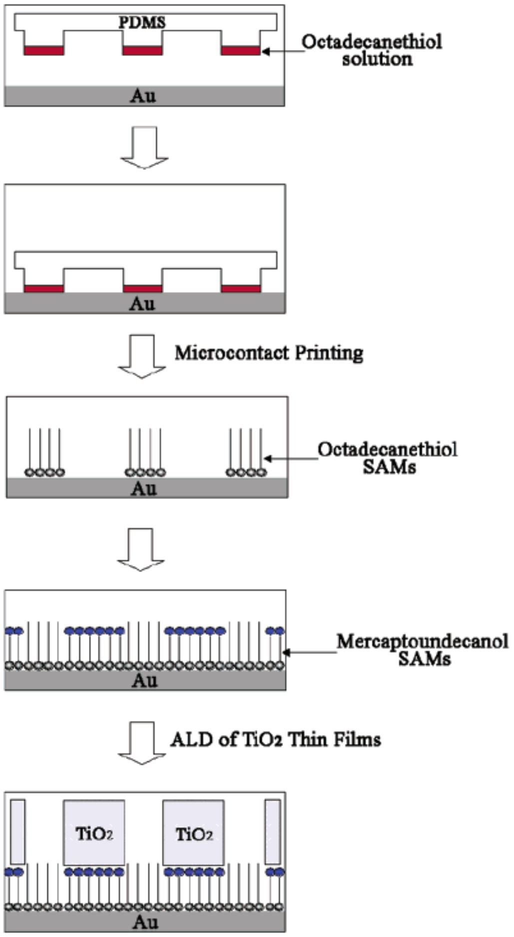

Figure 1. Schematic outline of the procedure to fabricate patterned TiO_2 thin films by using microcontact printing and selective atomic layer deposition.

and near-IR frequency, and high chemical stability.[19] They have been shown to be useful as antireflection coating, sensors, and photocatalysts.[20] The TiO_2 thin film is also a promising material for the development of microelectronics including as an alternative to silicon dioxide in the gate dielectric of metal oxide semiconductor field effect transistors (MOSFETS), due to its high dielectric constant.[15] Here we report a patterning method for TiO_2 thin films using microcontact printing of alkanethiolate SAMs on gold, followed by selective atomic layer deposition of the TiO_2. Our approach consists of three key steps, as shown in Figure 1. First, patterned CH_3-terminated alkanethiolate SAMs on gold were formed by using microcontact printing. Second, the remaining regions of gold were coated with OH-terminated alkanethiolate SAMs. Third, the TiO_2 thin films were selectively deposited onto the SAM-patterned gold substrate by atomic layer deposition.

Experimental Section

Materials. 1-Octadecanethiol [$CH_3(CH_2)_{17}SH$] (Aldrich; 98%), 11-mercapto-1-undecanol [$HOCH_2(CH_2)_{10}SH$] (Aldrich; 97%), ethanol (Aldrich; anhydrous, 99%), and [$Ti(OPr^i)_4$] (STREM Chemicals; 99.999%) were used as received. Poly(dimethylsiloxane) (Sylgard 184) was ordered from Dow Corning. Deionized water was purified with a Millipore Milli Q plus system, distilled over $KMnO_4$, and then passed through the Millipore Simplicity system.

Preparation of Gold Substrates. Gold substrates used in this research were prepared by evaporating 200 nm of gold onto silicon (100) wafers that were precoated with 10 nm of chromium to promote adhesion.

Preparation of SAMs. The freshly prepared gold substrates were immersed in a 2.5 mM solution of octadecanethiol (ODT) or mercaptoundecanol (MUO) dissolved in ethanol for 3 h. Monolayer deposition was carried out at room temperature. The samples were then ultrasonically washed in ethanol to remove excess reactants and dried with nitrogen. The quality of the monolayers was checked by XPS and water contact angle.

Preparation of TiO_2 Thin Films. The samples were introduced into the ALD system (Cyclic 4000, Genitech). The TiO_2 thin films were deposited onto the gold substrates using [$Ti(OPr^i)_4$] and water as ALD precursors. Ar served as both a carrier and a purging gas. The [$Ti(OPr^i)_4$] and water were evaporated at 80 and 20 °C, respectively. The cycle consisted of 2 s exposure to [$Ti(OPr^i)_4$], 5 s Ar purge, 2 s exposure to water, and 5 s Ar purge. The total flow rate of the Ar was 20 sccm. The TiO_2 thin films were grown at 100 °C under 2 Torr.

Preparation of Patterned SAMs. A patterned monolayer of CH_3-terminated alkanethiolate on the gold substrate was made by using microcontact printing. Masters were fabricated by using conventional photolithography or e-beam lithography to pattern resists on silicon wafers. The masters have parallel lines and spaces with dimensions from 5 to 0.5 μm. Poly(dimethylsiloxane) (PDMS) stamps were produced according to a previously reported procedure.[21-23] The PDMS stamps were inked with a 10 mM ethanol solution of ODT and dried with nitrogen. The stamp was placed in contact on the gold substrate for 5 s. The stamp was carefully peeled off and the substrate was blown dry with nitrogen. The ODT-patterned gold substrates were immersed in a MUO solution for 30 min to coat the remaining regions of the substrates with OH-terminated alkanethiolate SAMs.

Analysis Techniques. Atomic force microscopy (AFM) images of the samples were obtained on a PSIA XE−100 operating in tapping mode. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using the ESCALAB MKII. Water contact angles of the SAM samples were determined on a model A-100 Rame-Hart NRL goniometer in ambient air by using the sessile drop method. X-ray diffraction (XRD, Rigaku RU-200BH) analysis was carried out to determine the crystallinity of the TiO_2 films. The thickness of the TiO_2 thin films was measured by scanning electron microscopy (SEM, JEOL) and UV spectrophotometer (Scinco S-3100).

Results and Discussion

1. Atomic Layer Deposition of TiO_2 Thin Films. The TiO_2 thin films were grown on OH-terminated alkanethiolate SAM-coated gold substrate by atomic layer deposition using [$Ti(OPr^i)_4$] and water precursors at 100 °C. To verify that the growth mechanism is really self-controlled, the pulse time of the precursor was varied between 1 and 10 s. The film thickness per cycle is saturated when the pulse time exceeds 2 s, which indicates that the growth is self-controlled. Figure 2 shows the thickness of the TiO_2 thin films versus the number of ALD cycles. The growth of the TiO_2 film thickness is extremely linear relative to the number of cycles, indicating that the ALD conditions were suf-

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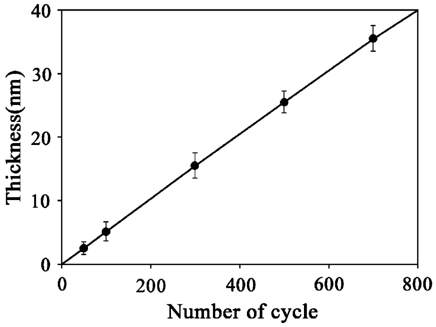

Figure 2. Thickness of the TiO_2 thin films versus the number of ALD cycles.

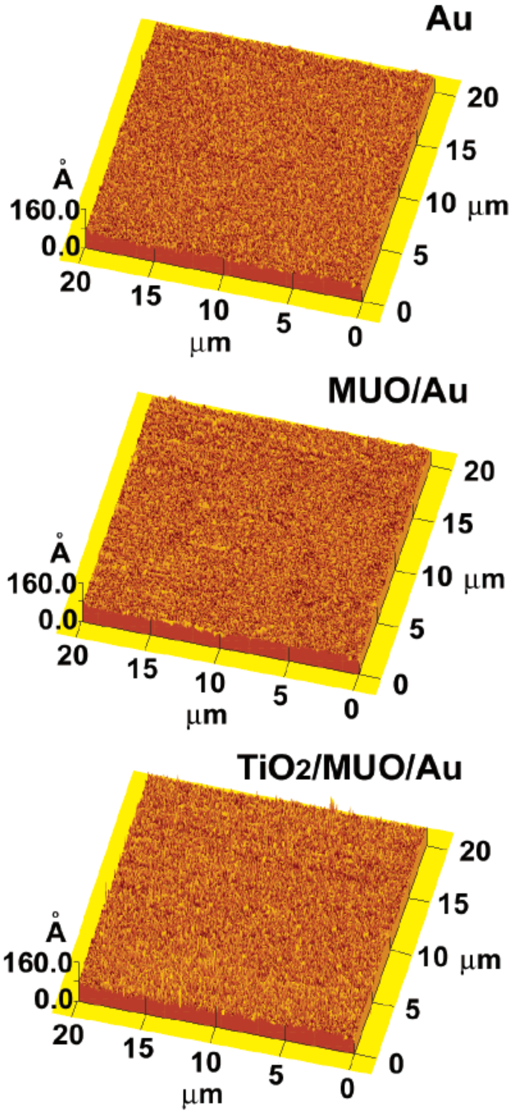

Figure 3. AFM images of clean gold substrate, MUO-coated gold substrate, and TiO_2 thin films deposited on MUO-coated gold substrate.

ficient for complete reaction. The measured growth rate was 0.51 Å per cycle. These results suggest that the TiO_2 ALD is self-controlled and that the ALD conditions are sufficient to complete reaction at 100 °C. The surface morphology of the TiO_2 films was examined by atomic force microscopy. The root-mean-square (rms) roughness of the TiO_2 surface is as low as 10.2 Å, as shown in Figure 3. In comparison, the rms roughnesses of the cleaned and MUO-coated gold substrates are about 9.8 and 9.9 Å, respectively. These results suggest that the surface morphology of the TiO_2 films grown at 100 °C is as smooth as the clean gold substrate.

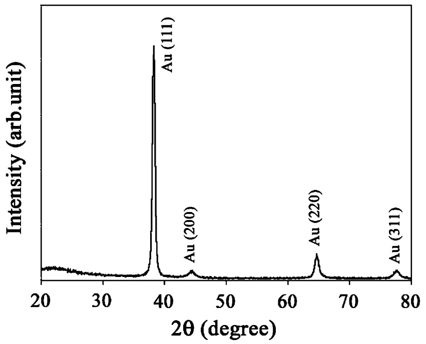

Figure 4. XRD pattern of TiO_2 thin film grown at 100 °C.

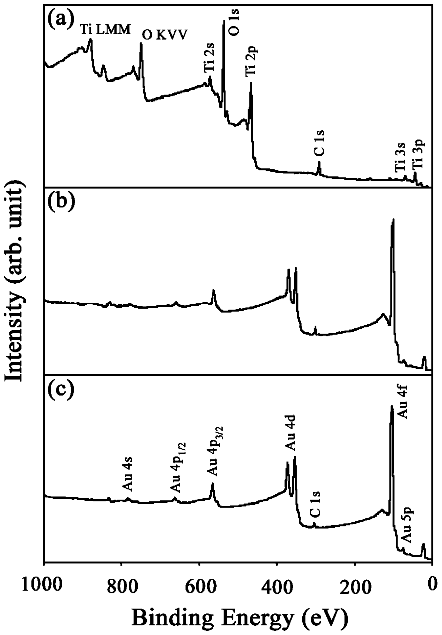

Figure 5. XP spectra of TiO_2 thin films deposited on (a) MUO-coated gold substrate, (b) ODT-coated gold substrate, and (c) clean gold substrate.

Figure 4 shows the XRD pattern for the TiO_2 thin film deposited on the MUO-coated gold substrate at 100 °C. The thickness of the TiO_2 film for XRD analysis was about 200 nm, which was thick enough to give us detectable XRD line intensities. Only the gold substrate peaks, however, were observed, indicating that an amorphous TiO_2 film was obtained at this temperature. XPS analysis was performed to determine the composition of the TiO_2 film deposited on the MUO-coated gold substrate at 100 °C. Figure 5a shows that the ratio of the areas under the Ti 2p and O 1s peaks of this film is the same as that of a TiO_2 single crystal. For comparison, the TiO_2 thin films were grown on the cleaned and ODT-coated gold substrates under the same ALD conditions. The TiO_2 thin films are not formed on these substrates because the substrate surfaces do not have any functional group to react with ALD precursors, as shown in Figure 5b,c. These observations indicate that the TiO_2 ALD on the OH-terminated alkanethiolate SAM-coated gold substrate at 100 °C is self-controlled and extremely linear relative to the number of cycles and that the TiO_2 thin films are amorphous and as smooth as the clean gold substrate.

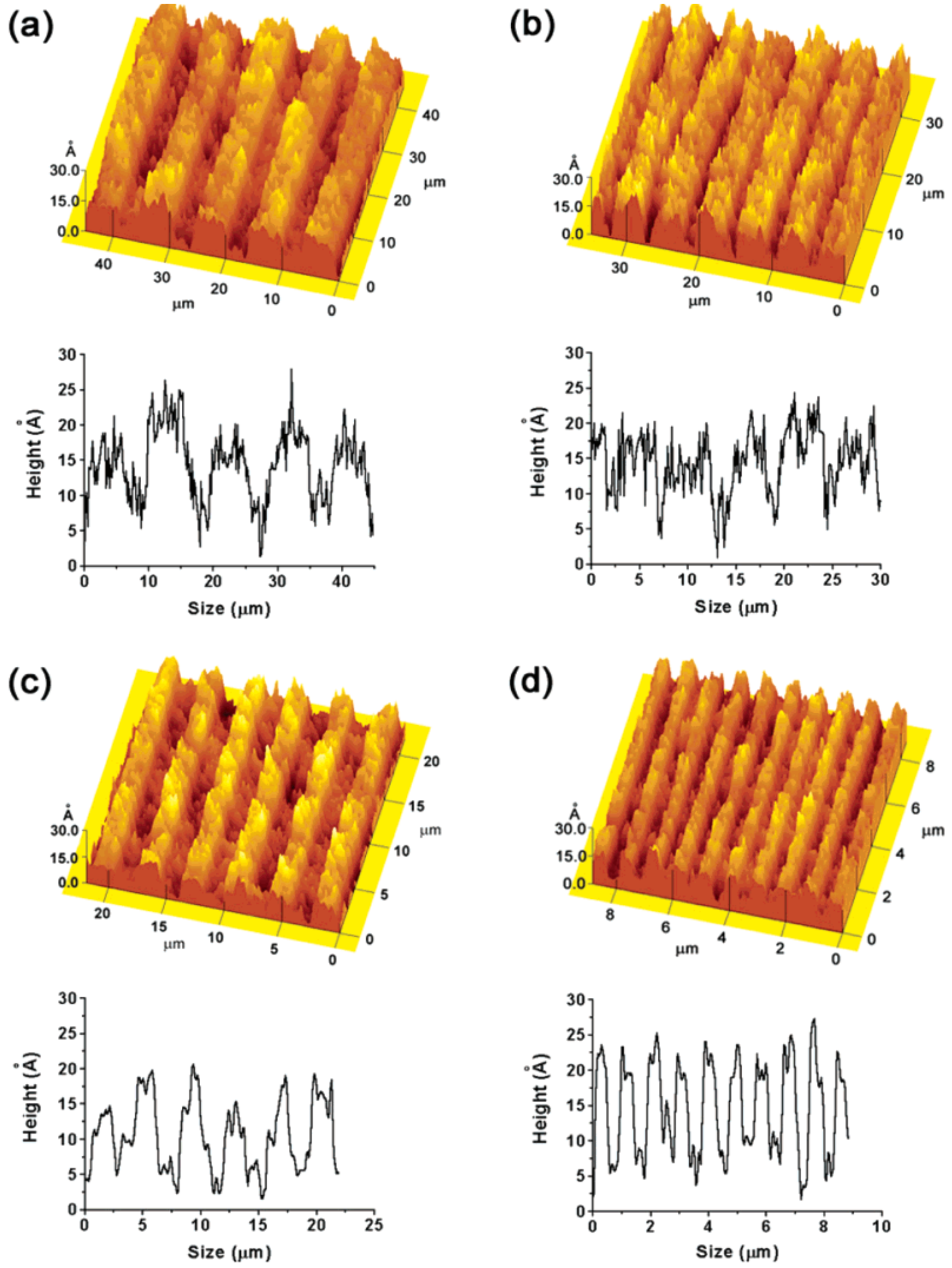

Figure 6. AFM images and cross sections of the patterned ODT monolayers generated by using microcontact printing on gold substrates: (a) 5.7 µm lines with 3.6 µm spaces, (b) 3.8 µm lines with 1.8 µm spaces, (c) 2.0 µm lines with 1.7 µm spaces, (d) 0.5 µm lines with 0.4 µm spaces.

2. Formation of Patterned SAMs Using Microcontact Printing. Patterned SAMs of the octadecanethiolate on the gold substrate were made by using microcontact printing. The masters we used for fabrication of stamps are silicon wafers with line-patterned resists, on scales from 5 to 0.5 µm. The masters with lines larger than 1 µm were fabricated using photolithography on silicon wafers, whereas high-resolution masters were fabricated using e-beam lithography. The stamps were fabricated by casting poly(dimethylsiloxane) (PDMS) on the masters. After curing, the PDMS stamps were peeled away from the masters. The PDMS stamps were inked with an ODT solution and then placed in contact with the gold substrate. When the stamps were made using these masters, the raised lines of the master corresponded to the recessed spaces of the stamps. When the ODT-patterned SAMs were made using these stamps, a negative, hydrophobic pattern of the original master was produced on the gold surface.

Parts a and b of Figure 6 show AFM images and cross sections of patterned SAMs fabricated by using the masters having 3.8 µm parallel lines with 5.5 µm spaces and 2.1 µm lines with 3.5 µm spaces, respectively. The patterned SAMs in Figure 6a have 5.7 µm lines with 3.6 µm spaces, and the SAMs in Figure 6b have 3.8 µm lines with 1.8 µm spaces. Parts c and d of Figure 6 show AFM images and cross sections of patterned SAMs fabricated by using the masters having 1.9 µm lines

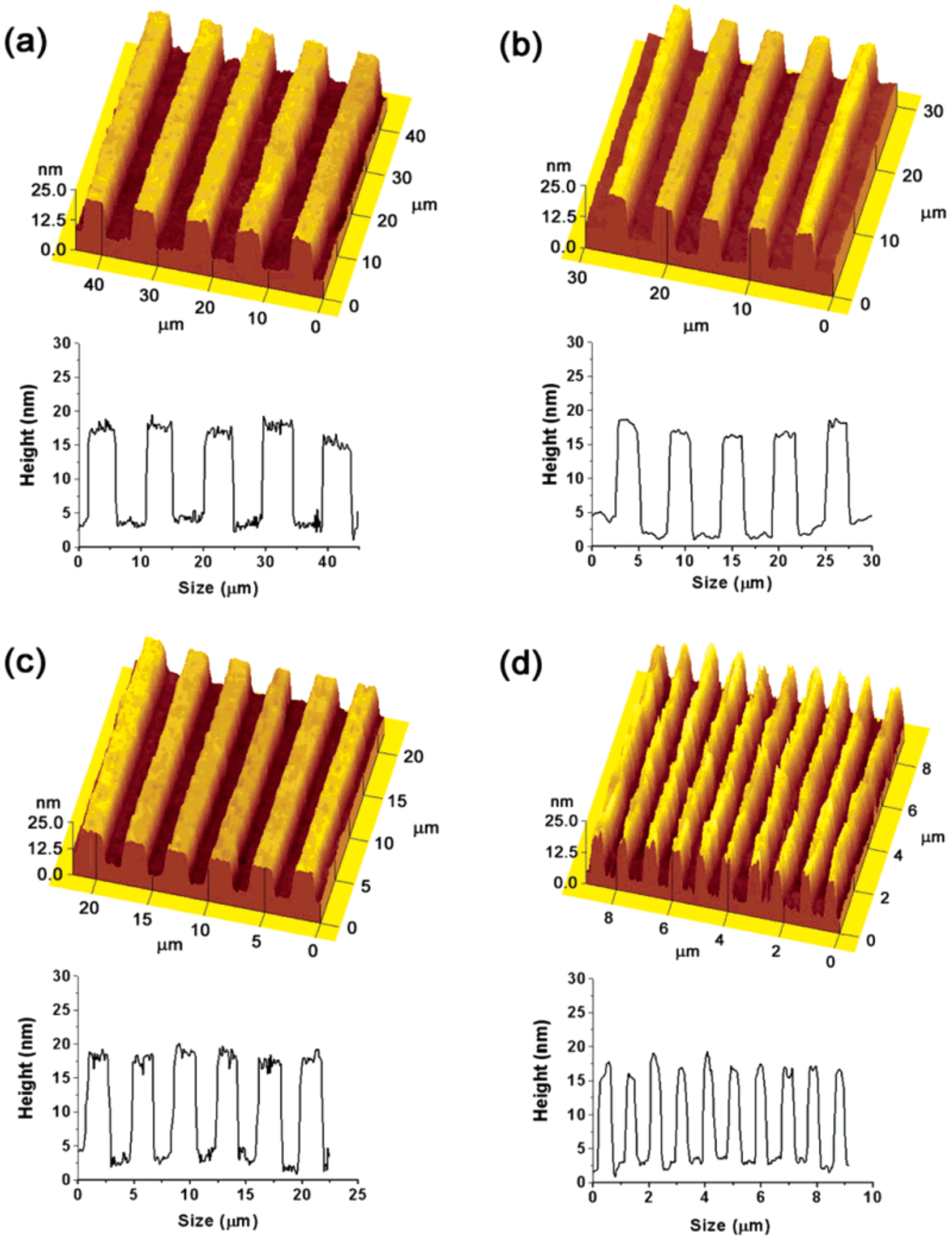

Figure 7. AFM images and cross sections of the patterned TiO_2 thin films generated by using selective ALD on the SAM-patterned gold substrates: (a) 3.7 μm lines with 5.6 μm spaces, (b) 1.9 μm lines with 3.7 μm spaces, (c) 1.8 μm lines with 1.9 μm spaces, (d) 0.5 μm lines with 0.4 μm spaces.

with 1.8 μm spaces and 0.4 μm parallel lines with 0.4 μm spaces, respectively. The patterned SAMs in Figure 6c have 2.0 μm lines with 1.7 μm spaces, and the SAMs in Figure 6d have 0.5 μm lines with 0.4 μm spaces. These images clearly show that the patterned monolayers retain the dimensions of the masters without noticeable line spreading. Additionally, the height of each patterned monolayer is about 23 Å, which is close to that of a densely packed ODT monolayer (~24 Å). The ODT-patterned gold substrates were then immersed in a MUO solution for 30 min to coat the remaining regions of the substrates with OH-terminated alkanethiol SAMs. The regions covered by CH_3-terminated SAMs formed from ODT are hydrophobic, low free-energy surfaces, whereas the regions exposing the OH-terminated alkanethiolate monolayers of the gold substrates are hydrophilic, high free-energy surfaces.

3. Selective Atomic Layer Deposition of TiO_2 Thin Films. The TiO_2 thin films were selectively deposited onto the SAM-patterned gold substrates by atomic layer deposition using $[Ti(OPr^i)_4]$ and water as ALD precursors. The selective ALD of the TiO_2 thin films was done at 100 °C and the number of ALD cycles in a run was kept 300. The thickness of the TiO_2 thin films, measured by AFM and SEM, is about 15 nm. Figure 7 illustrates AFM images and cross sections of micropatterned TiO_2 thin films, which were selectively deposited onto the monolayer-patterned gold substrate by ALD. The patterned SAMs showed high selectivity for TiO_2 ALD; hence, the patterns of the TiO_2 thin films were defined and directed by the patterned SAMs generated with microcontact printing. The TiO_2 thin films are selectively deposited only on the regions exposing the OH groups of the MUO-coated gold substrates, because the regions covered with the ODT monolayers do not have any functional group to react with ALD precursors. These AFM images clearly show that the patterned TiO_2 thin films retain the dimensions of the patterned SAMs used as templates with no noticeable line spreading.

Conclusions

We describe an atomic layer deposition of TiO_2 thin films on OH-terminated alkanethiolate monolayer-coated gold substrate at 100 °C. The ALD of the TiO_2 thin films is self-controlled and extremely linear relative to the number of cycles, and the TiO_2 thin films are smooth and amorphous. We also demonstrate a selective atomic layer deposition of TiO_2 thin films on patterned alkanethiolate self-assembled monolayers formed by microcontact printing. The atomic layer deposition offers an ideal method for selective deposition of thin films on patterned SAM-coated gold substrate, because the ALD process is very sensitive to the surface conditions of the substrates. The TiO_2 thin film is selectively deposited only on the regions of the gold substrates covered with the OH-terminated monolayers, because the regions covered with CH_3-terminated alkanethiolate monolayers do not have any functional group to react with precursors.

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