Selective Atomic Layer Deposition of Titanium Oxide on Patterned Self-Assembled Monolayers Formed by Microcontact Printing

Mi H. Park, Young J. Jang, Hyung M. Sung-Suh, and Myung M. Sung*

Department of Chemistry, Kookmin University, Chongnung-dong, Songbuk-ku, Seoul 136-702, Korea

We demonstrate a selective atomic layer deposition of TiO_2 thin films on patterned alkylsiloxane self-assembled monolayers. Microcontact printing was done to prepare patterned monolayers of the alkylsiloxane on Si substrates. The patterned monolayers define and direct the selective deposition of the TiO_2 thin film using atomic layer deposition. The selective atomic layer deposition is based on the fact that the TiO_2 thin film is selectively deposited only on the regions exposing the silanol groups of the Si substrates because the regions covered with the alkylsiloxane monolayers do not have any functional group to react with precursors.

Introduction

Thin films of titanium dioxide (TiO_2) have high refractive index, excellent transmittance in the visible and near-IR frequency, and high chemical stability.[1] They have been shown to be useful as antireflection coating, sensors, and photocatalysts.[2] 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.[3] Moreover, titanium oxide is a constituent of important multicomponent oxides such as $BaTiO_3$ and $SrTiO_3$, which are well-known to be ferroelectrics.[4]

Self-assembled monolayers (SAMs) are thin organic films which form spontaneously on solid surfaces. They have been shown to be useful as passivating layers and also for the modification of surface properties. Potential applications include wetting, adhesion, friction, chemical sensing, ultrafine scale lithography, and protection of metals against corrosion.[5-7] Several different varieties of SAMs have been investigated, including alkanethiols [$CH_3(CH_2)_{n-1}SH$] on Au, Ag, and Cu, and alkyltrichlorosilanes [$CH_3(CH_2)_{n-1}SiCl_3$] on SiO_2, Al_2O_3, and mica.[5] A key to utilizing SAMs in many advanced applications is the ability to pattern the monolayers.

High-resolution patterns can be formed by printing SAMs using soft lithography[8-10] or by decomposing SAMs using electron beams,[11] ion beams, photolithography,[12] or scanning probe microscopy.[13] A critical requirement for the use of patterned SAMs in advanced applications is the ability to generate them in the most economical, practical manner possible. Among these techniques for generating patterned SAMs, microcontact printing is the most practical because it is simple and rugged. This technique has been used to produce substrates for several different applications.[10,14,15]

Among various fabrication 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.[16,17] Selective depositions of thin films using chemical vapor deposition, electroplating, and electroless deposition have also been accomplished with patterned SAMs as templates. Atomic layer deposition (ALD) is a gas-phase thin film deposition method using self-terminating surface reactions. During the past decade, ALD has attracted considerable attention as a method of manufacturing high-quality thin films and producing tailored molecular structures.[18-20] 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 the ALD inherently eliminates gas-phase reactions. Elimination of gas-phase reaction results in emphasizing the importance of surface reaction. Since the ALD process is very sensitive to the surface conditions of the substrates, it offers an ideal method for selective deposition of thin films on patterned SAMs.

Here we report a patterning method of TiO_2 thin films using microcontact printing of alkylsiloxane SAMs, fol-

* To whom correspondence should be addressed. E-mail: smm@kookmin.ac.kr. Phone: 011-82-2-910-4767. Fax: 011-82-2-910-4415.

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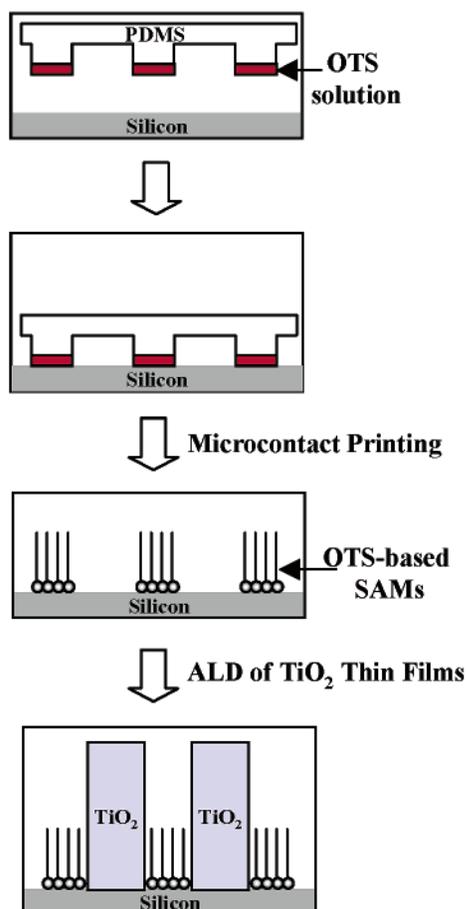
Figure 1. Schematic outline of the procedure to fabricate patterned TiO_2 thin films by using microcontact printing and selective atomic layer deposition.

lowed by selective atomic layer deposition of the TiO_2. Our approach consists of two key steps, as shown in Figure 1. First, the patterned alkylsiloxane SAMs were formed by using microcontact printing. Second, the TiO_2 thin films were selectively deposited onto the SAM-patterned Si substrate by atomic layer deposition.

Experimental Section

Materials. Octadecyltrichlorosilane [$CH_3(CH_2)_{17}SiCl_3$] (Aldrich, 97%), hexane (Aldrich, anhydrous, 99%), hexadecane (Aldrich, anhydrous, 99%), chloroform (Aldrich, anhydrous, 99%), and carbon tetrachloride (Aldrich, anhydrous, 99.5%) 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. [$Ti(OPr^i)_4$] (STREM Chemicals, 99.999%) was used as received.

Preparation of Si Substrates. The Si substrates used in this research were cut from n-type (100) wafers with resistivity in the range $1-5$ Ω cm. The Si substrates were initially treated with a chemical cleaning process, which involves degreasing, HNO_3 boiling, NH_4OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen, proposed by Ishizaka and Shiraki[21] to remove contaminants. A thin protective oxide layer was grown on the Si substrate by chemical oxidation with peroxysulfuric acid.

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 Si(100) 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 353 and 293 K, respectively. The cycle consisted of a 2 s exposure to
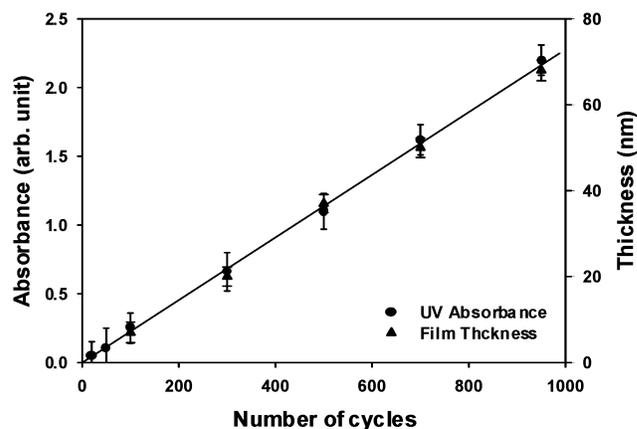
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Figure 2. UV absorbance and thickness of the TiO_2 thin films versus the number of ALD cycles.

[$Ti(OPr^i)_4$], a 5 s Ar purge, a 2 s exposure to water, and a 5 s Ar purge. The total flow rate of the Ar was 20 sccm. The TiO_2 thin films were grown at 423 K under 2 Torr.

Preparation of Octadecylsiloxane SAMs. Alkylsiloxane SAMs were formed by immersing the Si substrates in a 2.5 mmol solution of octadecyltrichlorosilane (OTS) precursor dissolved in hexadecane−chloroform (4:1). The samples were then washed in carbon tetrachloride to remove excess reactants and dried with nitrogen. The quality of the monolayers was checked by XPS and water contact angle. The water contact angle is about 110°, and the $^{1s}C/^{2p}Si$ peak area ratio measured by XPS is about 1.7.

Preparation of Patterned SAMs. A patterned monolayer of OTS on the Si 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 0.15 μm. Polydimethylsiloxane (PDMS) stamps were produced according to a previously reported procedure.[9,10,22] The PDMS stamps were inked with a 10 mM hexane solution of OTS and dried with nitrogen. The stamp was placed in contact on the Si substrate at 288 K for 30 s. The stamp was carefully peeled off, and the substrate was blown dry with nitrogen. The relative humidity was kept fixed at 60% in these experiments.

Analysis Techniques. Atomic force microscopy 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 SAMs 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) was carried out to determine the crystallinity of the TiO_2 films. The thickness of the TiO_2 thin films was measured by transmission electron microscopy (TEM, JEOL) and UV spectrometry (Scinco S-3100).

Results and Discussion

1. Atomic Layer Deposition of TiO_2 Thin Films. The TiO_2 thin films were grown on a Si(100) substrate by atomic layer deposition using [$Ti(OPr^i)_4$] and water at 423 K. 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. The UV absorbance and thickness of the TiO_2 thin films versus the number of ALD cycles are shown in Figure 2. The growth of the TiO_2 film thickness is extremely linear relative to the number of cycles, indicating that the ALD conditions were sufficient for complete reaction. The measured growth rate was 0.68 Å per cycle. These results suggest that the TiO_2 ALD is

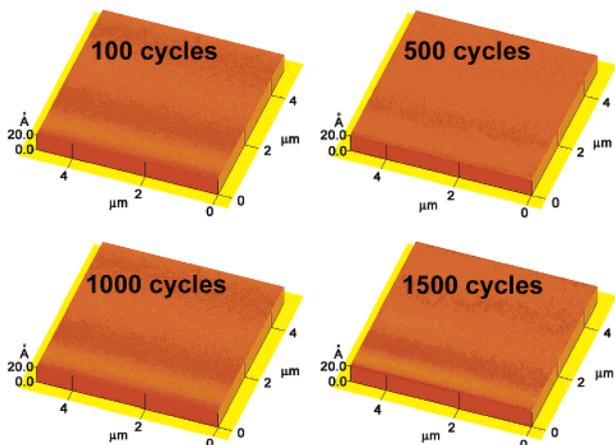(22) Wilbur, J. L.; Kumar, A.; Kim, E.; Whitesides, G. M. *Adv. Mater.* **1994**, *6*, 600.

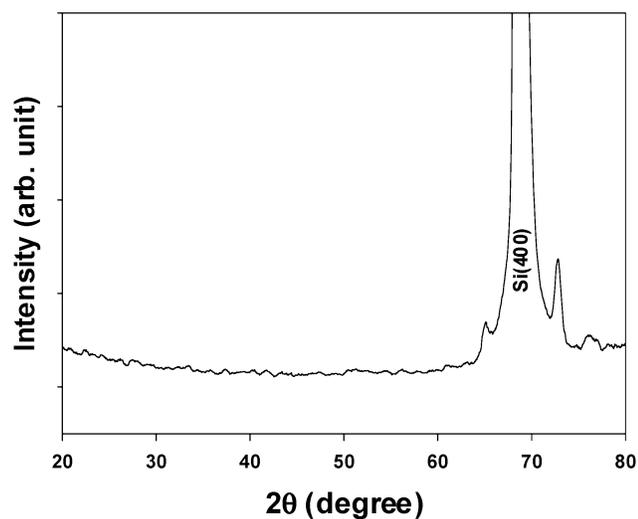**Figure 3.** AFM images of TiO$_2$ thin films versus the number of ALD cycles.

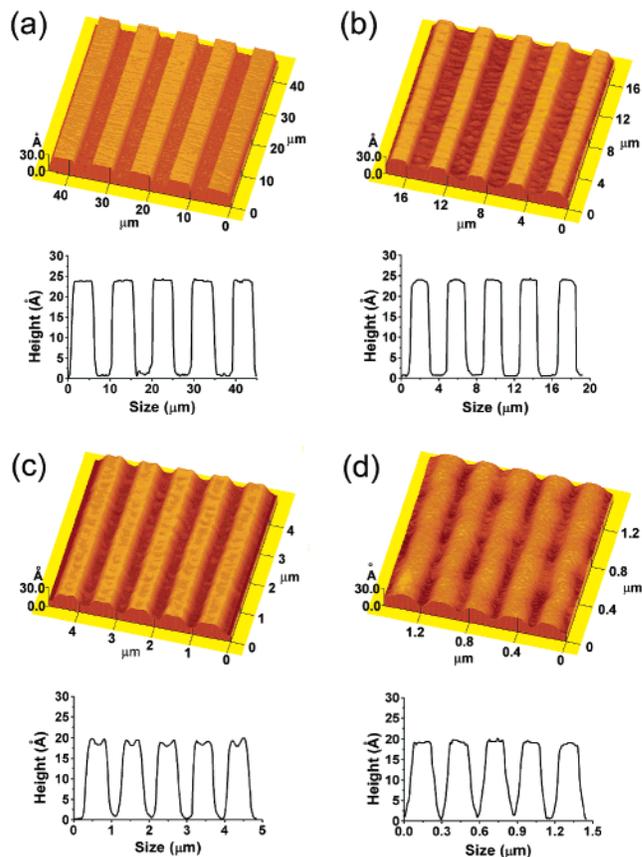**Figure 4.** XRD patterns of TiO$_2$ thin films grown at 423 K.

Figure 5. AFM images and cross sections of the patterned octadecylsiloxane monolayers by using microcontact printing on Si substrates.

self-controlled and that the ALD conditions are sufficient for complete reaction at 423 K.

Evolution of the surface morphology of the TiO$_2$ films was examined by atomic force microscopy (AFM) as the ALD cycle increased (Figure 3). Regardless of the number of the cycle, the surface morphology of the TiO$_2$ films is smooth and uniform, and the root-mean-square (rms) roughness of the surface is as low as 3.0 Å. In comparison, the surface roughness of the initial cleaned Si substrate is about 2.1 Å. Figure 4 shows the XRD pattern for the TiO$_2$ thin film on the Si substrate at 423 K. Only the Si substrate peaks were observed, indicating that an amorphous TiO$_2$ film was obtained at this temperature.

These observations indicate that the TiO$_2$ ALD is self-controlled and extremely linear relative to the number of cycles, and the TiO$_2$ thin films are smooth and amorphous at 423 K. For comparison, the TiO$_2$ thin films were grown on OTS-coated Si substrates at the same ALD conditions. The TiO$_2$ thin films are not formed on the OTS-coated Si substrate because the substrate surface does not have any functional group to react with ALD precursors.

2. Formation of Patterned SAMs Using Microcontact Printing. Patterned SAMs of the octadecylsiloxane on the Si 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 0.15 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 polydimethylsiloxane (PDMS) on the masters. After curing, the PDMS stamps were peeled away from the masters. The PDMS stamps were inked with an OTS solution and were placed in contact on the Si substrate. When the stamps were made using these masters, the raised lines of the master corresponded to the recessed spaces of the stamps. When patterned SAMs of OTS were made using these stamps, a negative, hydrophobic pattern of the original master was produced on the Si surface.

Parts a and b of Figure 5 show AFM images and cross sections of patterned SAMs fabricated by using the masters having 4.2 μm parallel lines with 5.5 μm spaces and 2.2 μm lines with 1.6 μm spaces, respectively. These images clearly show that the patterned monolayers retain the dimensions of the masters without noticeable line spreading. Additionally, the height of the patterned monolayer is about 24 Å, which is close to that of a densely packed octadecylsiloxane monolayer ($\sim$25 Å). The regions covered by SAMs formed from OTS are hydrophobic, low-free-energy surfaces, whereas the regions exposing the silanol groups of the Si substrates are hydrophilic, high-free-energy surfaces. Parts c and d of Figure 5 show AFM images and cross sections of patterned SAMs fabricated by using the masters having 400 nm lines with 550 nm spaces and 170 nm parallel lines with 130 nm spaces, respectively. The patterned SAMs in Figure 5c have 570 nm lines with 380 nm spaces, and the SAMs in Figure 5d have 180 nm lines with 120 nm spaces. These results indicate that the patterned SAMs almost retain the dimensions of the masters with slight line spreading. However, the height of the patterned monolayer is about
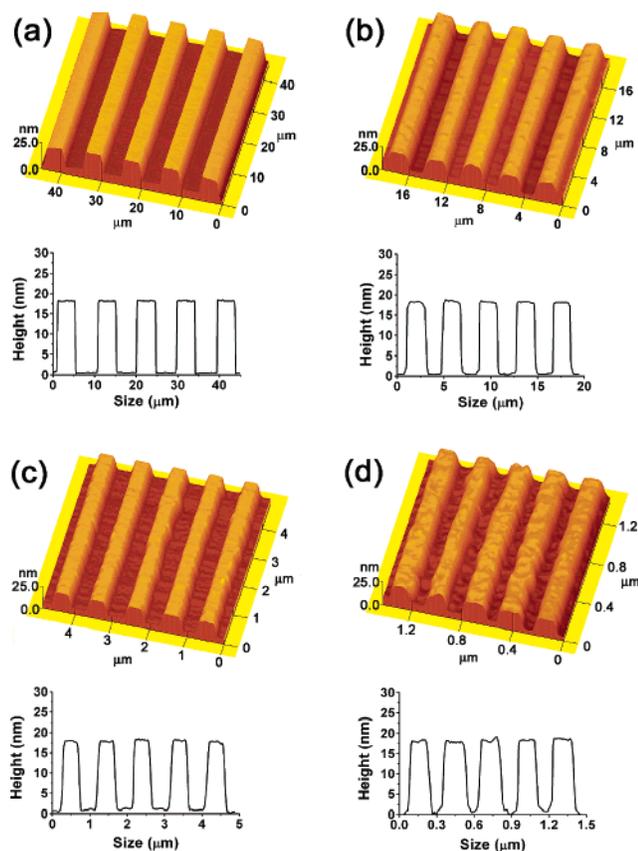
Figure 6. AFM images and cross sections of the patterned TiO$_2$ thin films by using selective ALD on the octadecylsiloxane SAM-patterned Si substrates.

20 Å, which is lower than that of the patterned monolayer on the micrometer scale.

3. Selective Atomic Layer Deposition of TiO$_2$ Thin Films. The TiO$_2$ thin films were selectively deposited onto the octadecylsiloxane SAM-patterned Si 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 423 K, and the number of ALD cycles in a run

was kept at 150. The thickness of the TiO$_2$ thin films, measured by AFM and TEM, is about 17 nm. Figure 6 illustrates AFM images and cross sections of micropatterned TiO$_2$ thin films, which were selectively deposited onto the monolayer-patterned Si substrate by ALD. 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 silanol groups of the Si substrates because the regions covered with the octadecylsiloxane 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 with no noticeable line spreading. Additionally, the patterned TiO$_2$ thin films on the submicrometer scale were also formed on the SAM-patterned Si substrates by atomic layer deposition, even though the height of the patterned SAMs was lower than that of a densely packed octadecylsiloxane monolayer.

Conclusions

We describe a selective atomic layer deposition of TiO$_2$ thin films on patterned octadecylsiloxane self-assembled monolayers formed by microcontact printing. The atomic layer deposition offers an ideal method for selective deposition of thin films on patterned SAMs 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 exposing the silanol groups of the Si substrates because the regions covered with the octadecylsiloxane monolayers do not have any function group to react with ALD precursors. 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 deposited at 423 K are smooth and amorphous.