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A New Patterning Method Using Photocatalytic Lithography and Selective Atomic Layer Deposition

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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 of the SAMs include wetting, adhesion, friction, chemical sensing, ultrafine scale lithography, and protection of metals against corrosion.[1−3] 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,[4−6] or by decomposing SAMs using electron beams,[7] ion beams, photolithography,[8] or scanning probe microscopy.[9] 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 various patterning methods, photolithography is the most practical, because it can transfer an entire pattern on a photomask to a SAM at a single time. Photolithography with alkanethiol SAMs has been done to obtain submicrometer spatial resolution.[10] However, there have been a few reports on UV photopatterning of alkylsiloxane SAMs in air. Previous studies have shown that the UV photopatterning of the alkylsiloxane SAMs requires relatively large amounts of energy because they are quite stable to UV irradiation of 254 nm, as compared to alkanethiolate SAMs.[11] Recently, we found that the monolayers are rapidly and homogeneously decomposed on a TiO_2 thin film under UV irradiation in air through the photooxidation of the alkyl chains.[12] Upon UV irradiation of 254 nm, the semiconductor TiO_2 can generate electron−hole pairs, and subsequently produce highly reactive oxygen species (e.g., OH, O_2 radicals) via electron scavenging by adsorbed O_2 and hole trapping by the surface OH^- or adsorbed H_2O.[13] These oxygen radicals can oxidize and decompose most organic compounds and some inorganic compounds. Considering its effectiveness for the photocatalytic decomposition of organic compounds,[14] TiO_2 photocatalysis can be a promising way to decompose the alkylsiloxane SAMs and can be ultimately applicable to the UV photopatterning of them.[15,16]

Among various fabrication techniques, 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.[17,18] 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 that uses self-terminating surface reactions. During the past decade, ALD has attracted considerable attention as a method for manufacturing high-quality thin films and producing tailored molecular structures.[19] 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 the gas-phase reaction results in emphasis of the importance of the surface reaction. Because the ALD process is very sensitive to surface conditions of the substrates, it is an ideal method for selective deposition of thin films on patterned SAMs.

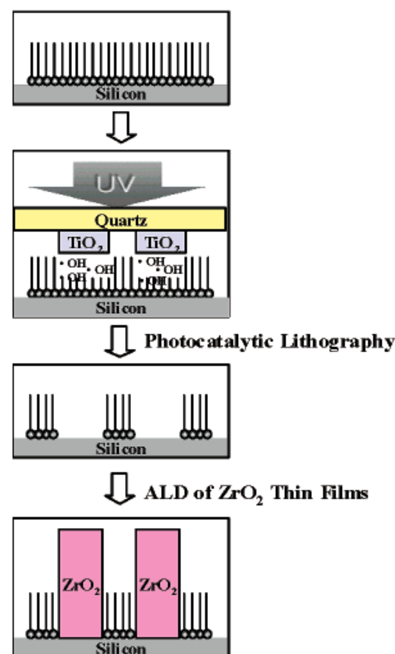

Figure 1. Schematic outline of the procedure to fabricate patterned thin films by using photocatalytic lithography and ALD.

Here, we report a new fabrication method using photocatalytic lithography of alkylsiloxane SAMs, followed by selective deposition of thin films using atomic layer deposition. Our approach consists of three key steps, as shown in Figure 1. First, the alkylsiloxane SAMs were formed by immersing Si substrate in alkyltrichlorosilane solution. Second, photocatalytic lithography using a quartz plate coated with patterned TiO_2 thin films was done to prepare patterned SAMs of alkylsiloxane on the Si substrate. Third, ZrO_2 thin films were selectively deposited onto the SAMs-patterned Si substrate by atomic layer deposition.

The octadecylsiloxane SAMs were formed by placing the oxidized Si substates in a 2.5 mmol solution of octadecyltrichlorosilane (OTS) precursor dissolved in 4:1 hexadecane/chloroform for 1 h. The samples were then washed in carbon tetrachloride to remove excess reactants and dried with nitrogen. The quality of the monolayers was checked by X-ray photoelectron spectroscopy (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.

Photodecomposition of the octadecylsiloxane SAMs in contact with TiO_2 thin films deposited on the quartz plates was studied using XPS and contact angle analysis. For comparison, photodecomposition of the SAMs in contact with SiO_2 of the quartz plate surface without the TiO_2 was also studied. The decomposition rate

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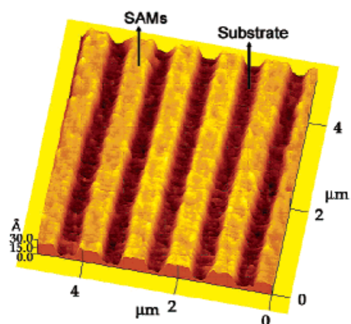

Figure 2. Three-dimensional AFM image (5 μm × 5 μm) for the patterned octadecylsiloxane monolayer by using photocatalytic lithography.

of the monolayers in contact with the TiO_2 thin films is 20 times faster than that in contact with the SiO_2 under UV irradiation in air. The octadecylsiloxane SAMs in contact with the TiO_2 are completely decomposed after 2 min of UV irradiation, whereas the monolayers in contact with the SiO_2 remain intact.

Patterned SAMs of the octadecylsiloxane on the Si substrate were made by using photocatalytic lithography. The quartz plate coated with patterned TiO_2 thin films having 400 nm parallel lines and 580 nm spaces was placed in contact on the SAMs-coated Si substrate. The SAMs-coated Si substrate was then exposed through the quartz plate to a 254 nm UV lamp for 2 min. Figure 2 shows an AFM image of patterned SAMs having 575 nm lines with 405 nm spaces, indicating that the patterned monolayer retains the dimensions of the TiO_2 pattern of the quartz plate 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 (~25 Å). This observation indicates that the monolayer regions contacted with the TiO_2 thin films of the quartz plate are completely decomposed during the first 2 min of irradiation and expose the silanol groups of the Si substrate. However, the monolayer regions not in contact with the TiO_2 of the quartz plate remain intact after 2 min of UV irradiation and still expose the methyl groups of the SAMs.

A ZrO_2 thin film was selectively deposited onto the octadecylsiloxane SAMs-patterned Si substrate by atomic layer deposition using $Zr[OC(CH_3)_3]_4$ and water as ALD precursors. Figure 3 illustrates the AFM image and cross section of patterned ZrO_2 thin films selectively deposited onto the monolayer-patterned Si substrate by ALD. The patterns of the ZrO_2 thin films were defined and directed by the patterned SAMs generated with photocatalytic lithography. The ZrO_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. The lines of the ZrO_2 thin films are 430 nm wide and separated by 550 nm, indicating that the patterned ZrO_2 retains the dimensions of the patterned SAMs without noticeable line spreading.

In summary, we describe a new patterning method using photocatalytic lithography of the alkylsiloxane SAMs and selective ALD of thin films. The photocatalytic lithography is based on the fact that the decomposition rate of the alkylsiloxane monolayers in contact with the TiO_2 is much faster than that with the SiO_2 under UV irradiation in air. The patterned SAMs of the octadecylsiloxane on the Si substrate were made by using the quartz plate coated with the patterned TiO_2 thin films under UV irradiation in air. These patterned SAMs define and direct the selective deposition of the ZrO_2 thin films using ALD.

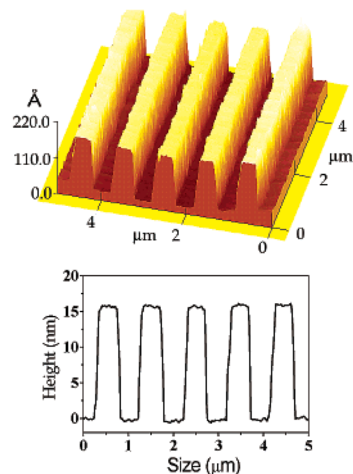

Figure 3. Three-dimensional AFM images (5 μm × 5 μm) and cross sections for the patterned ZrO_2 thin films fabricated by using photocatalytic lithography and ALD.

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Supporting Information Available: Details of materials, preparation of Si substrates, preparation of quartz plates coated with patterned TiO_2 films, photocatalytic lithography, preparation of patterned ZrO_2 films, and analysis techniques (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: Boston, MA, 1991.
(2) Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.
(3) Jennings, G. K.; Laibinis, P. E. *Colloids Surf., A* **1996**, *116*, 105.
(4) Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9188.
(5) Kumar, A.; Whitesides, G. M. *Appl. Phys. Lett.* **1993**, *63*, 2002.
(6) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1499.
(7) Carr, D. W.; Lercel, M. J.; Whelan, C. S.; Craighead, H. G.; Seshadri, K.; Allara, D. L. *J. Vac. Sci. Technol., A* **1997**, *15*, 1446.
(8) Huang, J. Y.; Hemminger, D. A. *Langmuir* **1994**, *10*, 626.
(9) Xu, S.; Liu, G. *Langmuir* **1997**, *13*, 127.
(10) Poirier, G. E.; Herne, T. M.; Miller, C. C.; Tarlov, M. J. *J. Am. Chem. Soc.* **1999**, *121*, 9703.
(11) Tao, Y.; Wynn, D.; Dudek, R.; Borguet, E. *Langmuir* **2001**, *17*, 4497.
(12) Lee, J. P.; Kim, H. K.; Park, C. R.; Park, G.; Kwak, H. T.; Koo, S. M.; Sung, M. M. *J. Phys. Chem. B* **2003**, *107*, 8997.
(13) Ishibashi, K.; Nosaka, Y.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem. B* **1998**, *102*, 2118.
(14) Fuhishima, A.; Honda, K. *Nature* **1972**, *238*, 37.
(15) Tatsuma, T.; Kubo, W.; Fujishima, A. *Langmuir* **2002**, *18*, 9632.
(16) Haick, H.; Paz, Y. *Chemphyschem.* **2003**, *4*, 617.
(17) Xia, Y.; Zhao, X.; Whitesides, G. M. *Microelectron. Eng.* **1996**, *32*, 255.
(18) Masuda, Y.; Jinbo, Y.; Yonezawa, T.; Koumoto, K. *Chem. Mater.* **2002**, *14*, 1236.
(19) Suntola, T. *Mater. Sci. Rep.* **1989**, *4*, 261.

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