

Nonlithographic Micro- and Nanopatterning of TiO₂ Using Polymer Stamped Molecular Templates

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The polymer-on-polymer stamping technique was used to template patterned TiO₂ onto polymer thin films. Polystyrene-*b*-polyvinyl pyridine diblock copolymer (PS-*b*-PVP) was stamped on a layer-by-layer assembled thin film of poly(allylamine hydrochloride) and poly(acrylic acid). After rinsing the surface with a good solvent for the block copolymer, an adsorbed PS-*b*-PVP monolayer remained on the polyelectrolyte film, resulting in a pattern of alternating hydrophobic and carboxylic acid containing hydrophilic regions. The surface was used as a template for the selective deposition of TiO₂ on the multilayer surface, using an acid-catalyzed hydrolysis of (NH₄)₂TiF₆. Using this novel approach, we have successfully demonstrated the patterning of TiO₂ film on a polyelectrolyte multilayer. Finally, nanoscale features consisting of 200 nm lines alternating with a 350 nm period was accomplished. This paper represents the first such attempt to create an all-polymer nonlithographic template for the directed deposition of TiO₂ or related metal oxides; this technique, which utilizes the versatile polyelectrolyte multilayer process, enables the construction of complex polymer-inorganic microstructures suitable for electrooptical and photonic applications.

Introduction

The layer-by-layer approach to thin film assembly permits the nanometer scale tuning of composition and functionality for a vast range of applications,¹ including electrooptic,² electroluminescent,³ conducting,⁴ and dielectric films; further, a broad range of materials systems can be incorporated into these films, such as organic⁵ and inorganic nanoparticles,⁶ with nanometer level control over film thickness and morphology. Recent applications of layer-by-layer polyelectrolyte films have extended to biological systems.⁷ To be able to fully utilize polyelectrolyte multilayer techniques for the formation of devices, sensors, and displays, it is necessary to be able to pattern additional material components atop existing multilayer thin films. Of key interest is the ability to integrate organic and inorganic patterned materials in a polymer multilayer structure using inexpensive processing techniques that allow easy implementation into low cost devices. Of particular importance are methods that are compatible with the use of soft or flexible substrates, such as plastic substrates, optical fibers, or even nonwoven fabrics.

On the other hand, the deposition and patterning of metal oxides on various substrates has become a rapidly growing research area because of the potential of flexible electronics.⁸ Current approaches to patterning oxides normally involve deposition by a vapor-phase technique,

followed by postdeposition etching. This method presents difficulties with respect to uniform etching and thermal stability of substrate. One strategy instead of deposition by a vapor-phase technique to deposit metal oxides on substrates is using the functional group on the self-assembled monolayers (SAMs). Using this approach, uniform and adherent metal oxide thin films are deposited.^{9–20} Microcontact printing of SAMs can define and direct the patterned deposition of metal oxide thin layers on substrates.^{21–24} Microcontact printing of SAMs is viable for Au, Si, and glass substrates but is not directly applicable to a broad range of plastic surfaces. It is desirable to extend this technique to the patterning of polymer substrates to realize the goal of flexible plastic electronics.

Previously, we demonstrated the patterning of layer-by-layer polyelectrolyte films containing strong and weak polyions with high selectivity onto surfaces^{25–29} using

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microcontact printing³⁰ of surfaces as templates. The resulting patterned film systems can then be used as elements in devices and sensors and can also serve as surface templates for the further deposition of materials.^{31,32} These microfabrication techniques are of even greater interest if applicable to a range of substrates, including glass, plastic, and flexible substrates. For these reasons, we have demonstrated that by adapting the microcontact printing method to synthetic macromolecules, polymer-on-polymer stamping can be used to create chemically patterned polymer surfaces using the direct stamping of polyelectrolytes and copolymers.^{33,34} This technique, which is an adaptation of microcontact printing utilizing the transfer of polymer monolayers, can be used to chemically pattern a range of polymer surfaces, including the top surfaces of polyelectrolyte multilayers. An important asset to the approach is the ability to create alternating chemical surface regions on functional layer-by-layer polyelectrolyte films that can serve as a template for further materials deposition.

Here, we report for the first time the patterned functionalization of polyelectrolyte multilayer surfaces to template an inorganic oxide, titanium dioxide, using the direct transfer of a block copolymer template onto the multilayer surface. This process illustrates a key step toward the templating of inorganic materials atop polymer surfaces to form patterned polymer thin film composites without the use of SAM systems such as thiols or silanes that generally require a metal or metal oxide surface. Titanium dioxide (TiO₂) is an especially promising system for photocatalysis³⁵ and photovoltaic devices,³⁶ and its high refractive index and low scattering make it of interest for dielectric³⁷ and photonic band gap materials.³⁸ Moreover, because multilayers can be adsorbed on several substrates, including plastic, a flexible photovoltaic device or field effect transistor may be realized through the use of polymer stamping atop layer-by-layer polyelectrolyte films. This development is a general one that can be extended to the deposition of other oxides, metals, and inorganic materials on polymer surfaces for a range of applications. Several approaches such as alternate deposition of polyelectrolyte and metal oxides^{39,40} or continuous film deposition of TiO₂ on layer-by-layer polyelectrolyte film⁴¹ have been reported to create the composite of layer-by-layer polyelectrolyte films and metal oxides. Here, we

focused on the patterning of TiO₂ on the layer-by-layer polyelectrolyte film.

Layer-by-layer assembled films of poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) were used as the polymer substrate. The hydrophilic, acidic nature of PAA was used as a template of TiO₂ deposition from an aqueous bath of (NH₄)₂TiF₆ and boric acid. To pattern polyelectrolyte multilayer surfaces, polystyrene-*b*-polyvinylpyridine (PS-*b*-PVP) was stamped directly atop the film to create a patterned monolayer. The hydrophobic nature of the polystyrene block inhibits the deposition of TiO₂. We successfully produced a two-dimensional patterned thin film of TiO₂ with feature sizes from 5 μm down to less than 350 nm on layer-by-layer polyelectrolyte films.

Experimental Section

Materials. Polyelectrolytes: PAH with MW = 70000 (Aldrich) and PAA with MW = 50000–60000 (Polysciences) were used as the polycation and polyanion, respectively. In this report, a layer-by-layer film of PAH and PAA is described as (PAH_x/PAA_y)_m (where *x*, *y* are the pH values of polyelectrolyte solutions and *m* is the number of bilayers). Diblock copolymer: A polystyrene-*b*-polyvinylpyridine block copolymer (PS-*b*-PVP) with a PS block MW = 21400 and a PVP block MW = 20700 was purchased from Polymer Source. Stamp: The stamp used to make prints on the layer-by-layer film was a poly(dimethylsiloxane) (PDMS) stamp created using SYLGARD 184, DOW CORNING. Monomer for TiO₂ synthesis: The monomer used to synthesize TiO₂ was ammonium hexafluorotitanate (IV) ((NH₄)₂TiF₆) which was purchased from Aldrich.

Characterization. Film thickness was measured by a Tencor profilometer. Stamped features and patterned TiO₂ were observed by optical microscopy (LEITZ DMRX) and atomic force microscopy (AFM/Digital Instruments Dimension 3000). Contact angles were measured on a Rame-Hart goniometer (Rame-Hart Inc.) equipped with a video imaging system. Water drops were placed on three locations on the surface in the ambient environment and contact angles were measured on both sides of the drops. Contacting water drops were advanced and retreated with an Electrapipet (Matrix Technologies). X-ray photoelectron spectroscopy (XPS/Surface science SSX-100) was used to confirm the existence of TiO₂.

Method. Figure 1 contains a schematic of the procedure used to pattern the TiO₂ film.

Layer-by-Layer Film. The layer-by-layer film was prepared by alternate exposure to 20 mM solutions (on the basis of the molecular repeat unit of polymers). Film preparation was automated with a modified Carl Zeiss HMS DS slide stainer. Exposure time was 20 min per polymer solution, followed by 4-min Milli-Q water rinse. The top layer of the polyelectrolyte multilayer was PAA. The pH values of both solutions were 9.5, hereby designated (PAH_{9.5}/PAA_{9.5}). The number of bilayers was 20. After preparing the layer-by-layer film, substrates were dried with N₂ stream.

Stamping of PS-*b*-PVP Block Copolymer. Before stamping PS-*b*-PVP on (PAH_{9.5}/PAA_{9.5}), substrates were immersed into a pH = 9.5, 8, 6, or 2.5 buffer solution for pretreatment. A 10 mM PS-*b*-PVP/THF solution (concentration based on the formula weight of the nominal repeat unit of styrene and vinylpyridine) was used to ink PDMS stamps molded from lithographically prepared masters.⁴ After evaporation of solvent, the PDMS stamp was briefly dried under a N₂ stream and was brought into contact with the substrate for 10 min at room temperature. The excess PS-*b*-PVP is then rinsed away prior to the TiO₂ deposition step with a THF rinse, leaving a monolayer template for deposition of the oxide. (It is also possible to stamp the block copolymer, deposit the TiO₂ first, and then rinse off the excess block copolymer material after oxide deposition; however, this approach is only effective when the reagents used do not solvate the residual block copolymer. Contact angles were measured on the unrinsed, thick block copolymer transferred film, and very similar contact angles were found for these surfaces and the monolayers, indicating that the thicker film can also be used as a hydrophobic template if it remains stable during the desired processing conditions. We

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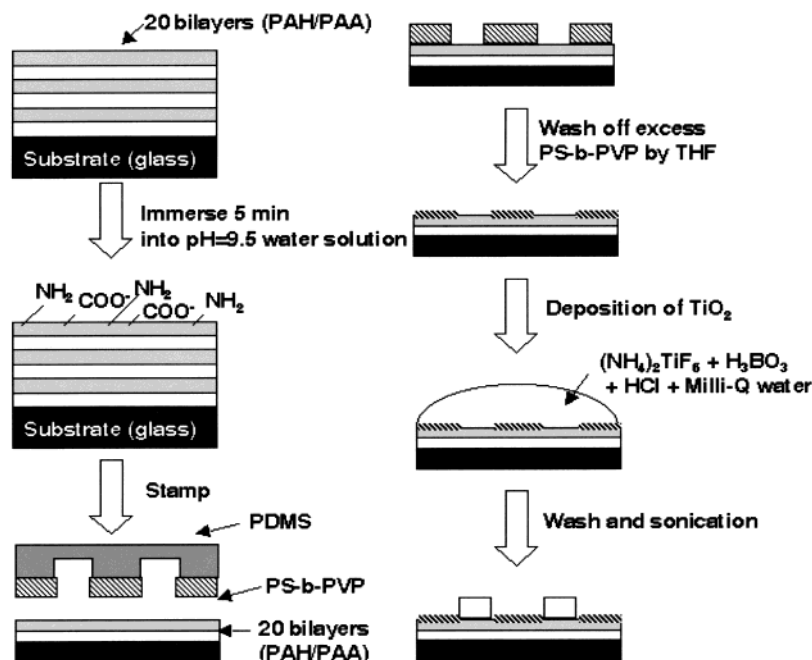


Figure 1. Schematic for patterning of TiO_2 film on layer-by-layer polyelectrolyte film.

found in these particular studies that suitable templating could be achieved with the rinse step in either order.)

Synthesis of TiO_2 Thin Film. TiO_2 thin films were synthesized onto layer-by-layer films as follows. $(\text{NH}_4)_2\text{TiF}_6$ and boric acid were dissolved separately in Milli-Q water and then mixed on a hot plate inside a disposable glovebag (Instruments for Research and Industry). Milli-Q water and HCl were added to regulate the synthesis conditions ($\text{pH} = 4.5$). The concentration of the $(\text{NH}_4)_2\text{TiF}_6$ and boric acid solutions were 0.02 M and 0.15 M, respectively. The substrate with the layer-by-layer film was immersed into the solution after the solution temperature reached 50°C . After 5–15 h, the substrate was washed with Milli-Q water, followed by 30 s of sonication.

Results and Discussion

Previous studies of polymer-on-polymer stamping by our group demonstrated the transfer of polystyrene-poly(acrylic acid) block copolymer to amino functional silicon oxide and polyelectrolyte multilayer surfaces.³⁴ In that case, binding of the second block was based on ionic interactions between acid and amine groups, and covalent bonding when treated at higher temperatures. For this study, a surface pattern of alternating hydrophobic and carboxylic acid groups was desired to realize the selective deposition of TiO_2 ; therefore, the direct transfer of PS-*b*-PVP to a carboxylic acid functional top multilayer surface was investigated. The stamping of PS-*b*-PVP was optimized for a $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ platform because multilayers adsorbed at this pH are highly stable to the TiO_2 bath conditions. At this pH, the PAH layers are expected to be thick because of the partial degree of ionization of primary amine groups; the resulting films therefore tend to have a relatively high surface concentration of amines even after adsorption of a PAA layer, which is highly ionized under these conditions, and thought to create somewhat thinner films at this pH. The thickness of a 20 bilayer film of $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ was 170 ± 8 nm; the average thickness of a single bilayer is 8.5 nm, which is a relatively thick layer. This single bilayer thickness is close to values of about 10 nm reported by Shiratori et al. for a single bilayer thickness of PAH/PAA at $\text{pH} = 9$.⁴² To determine individual layer thicknesses, we measured the thickness

of the PAH and PAA layers after depositing 10 bilayers of PAH/PAA and found that the PAH layer was 4.8 nm and the PAA layer was 3.7 nm, verifying the fact that the PAH layer was thicker. We confirmed that the number of free acid groups was relatively low on the multilayer surface through the use of a methylene blue stain, as utilized by Rubner and co-workers.⁴² Methylene blue dye stains carboxylic acid groups on the top multilayer surface, resulting in a blue color. We found that methylene blue left only a weak stain on the $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{10}$ surface, as opposed to the $(\text{PAH}_{7.5}/\text{PAA}_{3.5})_{10}$ surface, which was stained a deep blue color. In other words, the number of carboxylic acid groups on the top multilayer surface is relatively low, suggesting that amine groups permeate through the PAA top surface layer of $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{10}$ multilayers.

The $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ multilayer was treated with a buffer solution following assembly as a means of pretreatment prior to stamping. A range of pH values was used to examine the effect of the degree of ionization on the multilayer surface, and the transfer and adhesion of the PS-*b*-PVP after stamping. This effect is particularly important, as electrostatic or hydrogen-bonding interactions are highly dependent on the charged state of the functional groups.

Figure 2 contains optical micrographs of $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ stamped with PS-*b*-PVP following pretreatments at pH 2.5, 6, 8, and 9. Here, a stamp was used to transfer a PS-*b*-PVP pattern with a $3\ \mu\text{m}$ line width and a $15\ \mu\text{m}$ period; TiO_2 was selectively deposited on the larger alternate regions of the pattern (wide lines), and optical micrographs were taken normal to the surface. At all pH values of pretreatment, PS-*b*-PVP was transferred onto the $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ surface; however, the stability of the resulting monolayer and the quality of the stamped line feature as a template to deposition was influenced by the pH of the pretreatment solutions. When the pretreatment pH was 6 or lower, defects can clearly be observed in which the TiO_2 deposited beyond the multilayer hydrophilic regions and entered the boundaries of the stamped PS-*b*-PVP hydrophobic pattern. On the other hand, when the pH value of the pretreatment solution was 9.5, the resulting features were very clear and well-defined,

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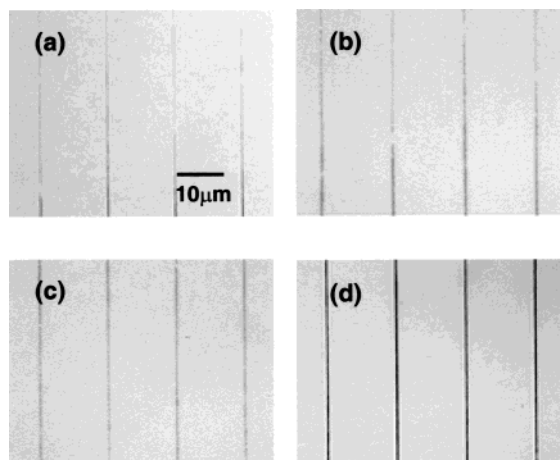


Figure 2. Optical microscope pictures of PS-*b*-PVP stamped (PAH/PAA)₂₀. (a) pretreated by pH = 2.5 solution, (b) pretreated by pH = 6 solution, (c) pretreated by pH = 8 solution, (d) pretreated by pH = 9.5.

Table 1. Thickness of Adsorbed PS-*b*-PVP on Pretreated (PAH/PAA)₂₀

pH of pretreatment solutions	thickness of PS- <i>b</i> -PVP	
	before rinse off (nm)	after rinse off (nm)
2.5	74 ± 6	4.6 ± 1.0
6	69 ± 11	3.8 ± 1.6
8	79 ± 7	5.1 ± 1.1
9.5	82 ± 8	5.2 ± 1.0

indicating the generation of TiO₂ film only within the hydrophilic regions of the surface.

Table 1 gives the thickness of the transferred PS-*b*-PVP film on the (PAH_{9.5}/PAA_{9.5})₂₀ surface after pretreatment with different pH solutions before and after rinsing the surface with THF to remove excess polymer. In general, the amount of total polymer initially transferred ranges from 70 to 80 nm. The thickness of the rinsed samples indicates the amount of PS-*b*-PVP truly adsorbed to the (PAH_{9.5}/PAA_{9.5})₂₀ surface, resulting in the monolayer thin film that acts as a template to deposition. The PS-*b*-PVP monolayer thicknesses, which ranged from 4 to 5 nm, exhibited maximum values at surface pretreatment pH values of 8 and 9, when the amines are in their basic unprotonated state. The higher quality of the stamped PS-*b*-PVP monolayer was at higher pH pretreatments, as indicated by film thickness and templating results, suggesting that the block copolymer may be more closely packed on the surface under these conditions, yielding a denser polystyrene surface layer that acts as a more effective resist.

Several possible multivalent adhesive interactions can dominate the polymer stamping process: ionic interactions, polar–polar interactions, hydrogen bonding, and covalent bonds. Because PS-*b*-PVP is dissolved in THF, and the pyridine group is not ionized under these conditions, electrostatics do not play a major role in adhesion, but both polar–polar attractions and hydrogen bonding are important in this case. On the surface of the (PAH_{9.5}/PAA_{9.5})₂₀ film, both carboxylic acid and amine functional groups exist.⁴² When the pH value is low, at 2.5, the amine groups, which have a p*K*_a of 9.0, are highly ionized. At this condition, hydrogen bonding between the carboxylic acid group of PAA and pyridine group of PS-*b*-PVP is likely to be dominant. When the pH value is high (8 or 9.5), the carboxylic acid group, which has a p*K*_a of 5.0, is highly ionized; hydrogen bonding between the amine

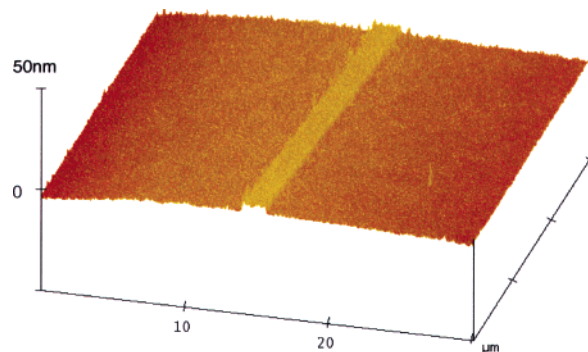


Figure 3. AFM profiles of PS-*b*-PVP stamped (PAH_{9.5}/PAA_{9.5})₂₀ after rinsing with THF to achieve truly adsorbed monolayer. Thickness of the monolayer is approximately 5.2 nm.

of PAH and pyridine groups of PS-*b*-PVP is more likely to be dominant. When the pH value is 6, both the carboxylic acid and the amine groups both have a strong ionic nature, and hydrogen-bonding interactions are likely to be weak.

From the images in Figure 2, it is clear that complete transfer of the stamped layer is not achieved at low or moderate pH. The optimal pattern transfer was achieved under conditions that favor hydrogen bonding between the pyridine group of PVP and the amine group of PAH, which is the dominant adhesive interaction for the surface when pretreated at pH = 9.5 so that the primary amines are in their reactive, unprotonated state. Both amine groups from PAH and carboxylic acid groups from PAA exist on the pretreated (PAH_{9.5}/PAA_{9.5}) surface because the PAA layers adsorb to form relatively thin layers at high pH. Because of the dense underlying polyamine film, a large number of free amine groups should be present on the surface, even when the PAA layer is on top. Because the surface contains such a large concentration of amine versus acid groups, the number of adhesive contacts possible for the PS-*b*-PVP block copolymer is greater under conditions that favor N–H–N hydrogen bonding than under conditions that favor COOH–N hydrogen bonding. The result is that monolayers of PS-*b*-PVP are much more stable on surfaces with unprotonated amine groups present.

Figure 3 shows an AFM image of the PS-*b*-PVP copolymer stamped onto the (PAH_{9.5}/PAA_{9.5})₂₀ after rinsing with THF. A PS-*b*-PVP copolymer monolayer remains adhered to the surface; the thickness of PS-*b*-PVP was 5.2 ± 1 nm after rinsing, consistent with the presence of a single monolayer of adsorbed polymer. The PS block resides as a hydrophobic glassy amorphous layer on the multilayer surface, whereas the PVP is adsorbed to the surface. A high resolution image is obtained after rinsing, indicating the fidelity of the stamping method and the ability to attain a well-defined monolayer on the surface. These findings are consistent with previous studies of polymer-on-polymer stamping, for which we found that only an adsorbed polymer monolayer remains on the polyelectrolyte surface after rinsing in the case of graft and block copolymers and polyelectrolytes.³⁴ The contact angle of a single continuous stamped monolayer of block copolymer was measured. The advancing and receding water contact angle of the stamped region was 74° and 70°, respectively, while it was 33° and 27° on the nonstamped region. The low degree of hysteresis between advancing and receding measurements suggest a very smooth monolayer surface, as evident in the AFM image in Figure 3. A chemically patterned hydrophilic acid surface with alternating hydrophobic polystyrene surface regions that resist deposition of TiO₂ was obtained by the

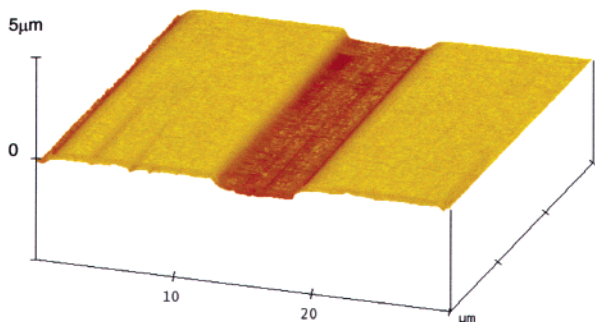


Figure 4. AFM profile of TiO_2 deposited on PS-*b*-PVP stamped $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$. The excess PS-*b*-PVP was rinsed by THF before TiO_2 deposition. The stamped feature size was 5 μm .

stamping of PS-*b*-PVP using a PDMS stamp, followed by immersion of the stamped substrate in a TiO_2 synthesis bath based on $(\text{NH}_4)_2\text{TiF}_6$ and boric acid, as described in the Experimental Section. The thickness of the TiO_2 film was controlled by adjusting the reagent concentration, substrate immersion time, and reaction temperature. The PS-*b*-PVP transferred film acted as an effective resist to the deposition of TiO_2 , resulting in TiO_2 deposited only on the hydrophilic acid surface area. The presence of the TiO_2 on the PAA surface of the $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ film was confirmed by X-ray photoelectron spectroscopy using a takeoff angle of 75° ; the atomic concentration of the deposited TiO_2 layer was $\text{Ti}/\text{O}/\text{C}/\text{N} = 25.74/47.84/24.12/1.22$. The ratio of titanium to oxygen is appropriate for TiO_2 , and the presence of carbon and nitrogen is likely due to contaminants from the atmosphere and multilayer substrate. A small amount of fluorine (atomic concentration of 1.08) was also detected as residual reagent left from synthesis.

In comparison, the atomic concentration of the surface regions stamped with the block copolymer after immersion in the TiO_2 was $\text{O}/\text{C}/\text{N} = 1.03/96.82/2.15$. The titanium concentration on the block copolymer surface was lower than the detection limits of the instrument. The high carbon content is consistent with a dense monolayer of hydrocarbon from polystyrene. The nitrogen content is due to the PVP block and the presence of amine groups at the top surface layer of the underlying multilayer. At the angle used for data collection, the penetration depth of the AFM is close to the thickness of the block copolymer monolayer. As shown by the XPS results, TiO_2 can be deposited on the $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ surface effectively with very high selectivity.

Figure 4 shows an AFM profile of a PS-*b*-PVP templated TiO_2 film deposited on a $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ film. The TiO_2 was deposited after rinsing off excess PS-*b*-PVP by THF. The total thickness of the TiO_2 film in this example was 1.2 μm . As shown in Figure 4, the TiO_2 deposited only on the nonstamped area, which is the $(\text{PAH}_{9.5}/\text{PAA}_{9.5})_{20}$ surface; this indicates that, as expected and confirmed with XPS, the hydrophobic PS monolayer formed using polymer-on-polymer stamp acts as an effective resist to oxide deposition. Optical microscopy images of the resulting patterned TiO_2 film are shown in Figure 5. TiO_2 deposited onto the surface template to yield clean patterns with well-defined edges and little or no defects. In Figure 5a, the TiO_2 appears as bright lines exhibiting different colors because of the interference of light. The patterned features shown are 1, 1.5, 2, 3, and 5 μm width line features. On the other hand, in Figure 5b, the TiO_2 was deposited on the outer regions of dot features with 1, 1.5, and 3 μm diameters. In the larger diameter circles (3 μm), TiO_2 could not be deposited completely on the edges of the

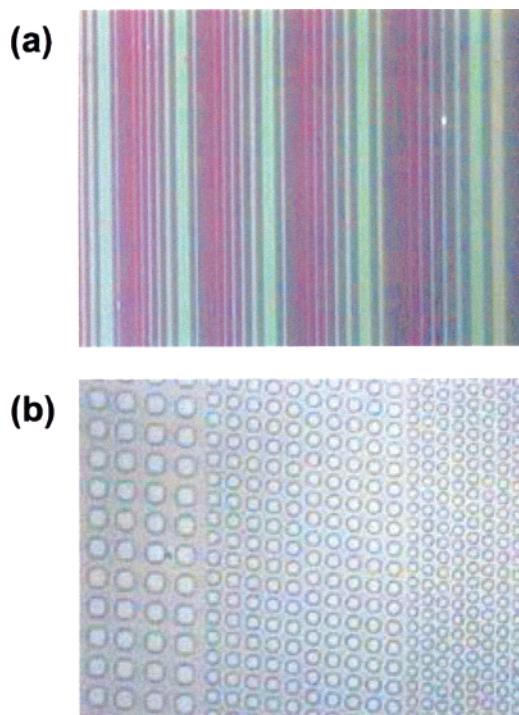


Figure 5. Optical micrographs of patterned TiO_2 film. (a) Linear patterned TiO_2 film, the line width of line features are 1, 1.5, 2, 3, and 5 μm . (b) Circular patterned TiO_2 film, the diameter of circle features are 1, 1.5, and 3 μm .

circles because the optimized immersion times for TiO_2 deposition differ from 1 μm to 3 μm diameter features; longer reaction times are necessary to complete larger features. For this reason, the features of the 3 μm diameter circles appear to have squared corners. This suggests that film growth nucleates and expands laterally from the center of the multilayer regions toward the edges of the patterns. The thickness of the TiO_2 film was about 500 nm in all cases shown in Figure 5.

Although electrostatic interactions between the protonated carboxylic acid group and TiO_2 do not exist, a strong adhesive nature was achieved on these surfaces. Shin et al. proposed that the reaction between a Ti sol-gel monomer and OH-terminated self-assembled monolayer (SAM) occurred via a ligand exchange reaction of the SAM's OH sites with Ti sol-gel monomer.¹⁰ In our case, the same mechanism might apply, because we found that when TiO_2 was deposited on a simple amine functionalized surface, the film was not stable and was easily removed upon washing with THF; on the other hand, an acid SAM will promote deposition with strong adhesive characteristics. In aqueous solutions, the hydrolysis of $[\text{TiF}_6]^{2-}$ with reactions 1 and 2 has been proposed by Schmitt et al.⁴³ H_3BO_3 reacts readily with F^- ions to give the more stable BF_4^- ion.



A ligand exchange reaction between the carboxylic acid group of $(\text{PAH}_{9.5}/\text{PAA}_{9.5})$ with $[\text{TiF}_6 - n(\text{OH})]^{2-n}$ might occur. Following this exchange between the carboxylic acid group and Ti sol-gel monomer, it is proposed that the TiO_2 is deposited and grown via the dehydration of the Ti sol-gel monomer.

(43) Schmitt, R. H.; Glove, E. L.; Brown, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 5292.

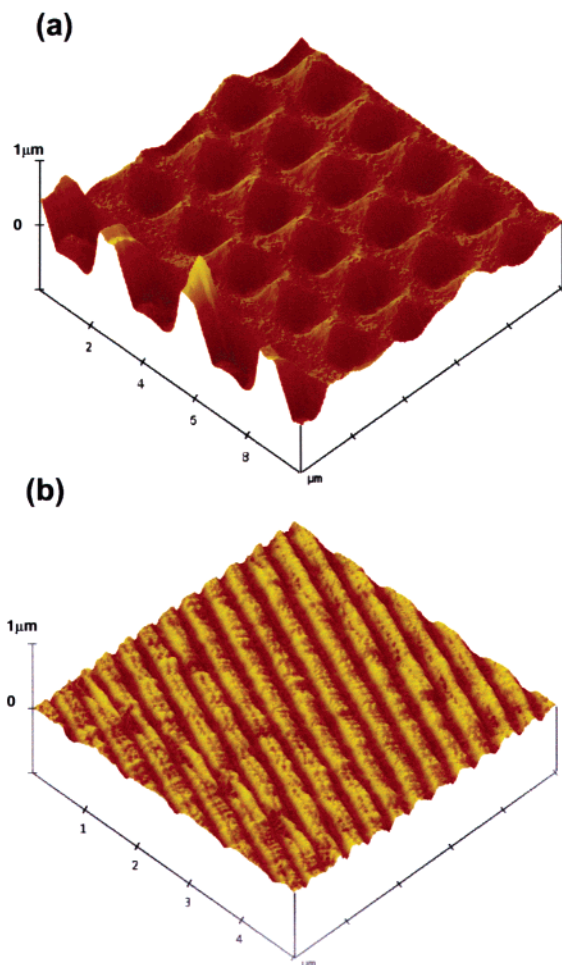


Figure 6. AFM images of nanopatterned TiO_2 film. AFM image was measured using tapping mode. (a) Circular patterned TiO_2 film, with the circle feature diameter at 950 nm. (b) Linear patterned TiO_2 film, the width of line feature is 350 nm.

The quality of the patterned TiO_2 film was controlled by tuning the surface roughness of the layer-by-layer polyelectrolyte film that was used as a platform. When a $(\text{PAH}_{7.5}/\text{PAA}_{3.5})$ multilayer was used as the substrate, the resulting TiO_2 film was rough and exhibited several cracks. This observation is because the rms roughness of the $(\text{PAH}_{7.5}/\text{PAA}_{3.5})$ film of 2.5 nm (on the basis of AFM) is relatively larger than the roughness of $(\text{PAH}_{9.5}/\text{PAA}_{9.5})$ multilayer at 0.3 nm; thus, the surface roughness of the layer-by-layer film strongly affects the quality of the TiO_2 deposited layer.

Once the ability to template micropatterned TiO_2 films on the multilayer surface was successfully established, we began to investigate nanoscale patterning of the TiO_2 film. PDMS stamps with periodic arrays of circle and line features were prepared from masters created using interference lithography.⁴⁴ Figure 6 shows a nanopatterned TiO_2 film; the diameter of the circular features are 950 nm, and the line width of the line features are 350

nm. The pattern was transferred in a HEPA filtered environment utilizing a mechanical support stand to apply controlled pressure on the stamp; details of this approach to nanoscale stamping have been published in a separate paper.⁴⁵ The PS-*b*-PVP block copolymer was successfully transferred to the multilayer surface and used to template TiO_2 patterns as described above. The feature sizes of the dot patterned TiO_2 film and the line patterned film were approximately 800 nm and 350 nm, respectively. The left side of the circular patterned features contains larger features of 1.5 μm . To our knowledge, this is the first demonstration of nanopatterned TiO_2 films templated onto polymer surfaces using nonlithographic techniques; moreover, the underlying layer of the patterned TiO_2 is a layer-by-layer film that can exhibit several functionalities, and novel optical and electrical devices can thus be readily realized.

Conclusion

In conclusion, we have demonstrated the concept of micro- and nanopatterning of TiO_2 film on polymer films using polymer-on-polymer stamping of block copolymers as a template. This technique is promising for novel optical and electronic devices such as selective reflection filters, microelectronic and microphotonic circuits, and photovoltaic devices with various kinds of substrates, including plastic. Further details of this procedure will be presented in a separate publication.^{46,47} The shape and size of two-dimensional patterned TiO_2 films were controlled by a stamped monolayer template, and TiO_2 film thickness was controlled via reaction time. Using this technique, we can systematically control the size, shape, and precise positioning of patterned TiO_2 elements on a surface. This technique can lead to the development of photonic waveguide devices, photovoltaic devices, and photocatalysis systems, as well as other complex optical and optoelectrical systems that need well-defined positioning such as photonic chips.⁴⁸ Layer-by-layer film can be adsorbed not only on glass substrates but on polymer substrates such as flexible polyester (Mylar), polystyrene, and polysiloxanes. Ongoing work involves the incorporation of these films in ultrathin photovoltaic devices. We believe that this technique provides an important new technological approach in the area of plastic electronics and photonics.

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