Micropattern Formation by Molecular Migration via UV-induced Dehydration of Block Copolymers

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A novel UV lithographic technique for the patterning of the block copolymer (Pluronic) thin films is developed. The present method is based on UV-induced water affinity changes in block copolymer films. By water vapor post-treatment of the film, a difference in water content is established between UV illuminated and unilluminated sections, which can induce an osmotic pressure at the interface. This osmotic pressure drives the migration of Pluronic molecules, resulting in formation of patterns on the block copolymer films. Remarkably, this patterning method requires neither initiators nor polymerizable moieties which are essential for a conventional photolithographic approach. Additionally, the etching process is bypassed, eliminating the use of destructive acids or organic solvents and making this an environmentally friendly patterning protocol. It is reported that Pluronic is photo-responsive to UV exposure, which causes the dehydration of the PEO-PPO-PEO backbone.

1. Introduction

In this era of portability and rapid technological advances, polymers with two or more different polymer chains linked together (block copolymers) can potentially offer an affordable solution for a variety of technological challenges.[1] In addition to the intrinsic functional properties block copolymers possess, controlled architectures of highly dense arrays of nanostructures can be designed and achieved which would otherwise be difficult to create with conventional lithographic techniques.[2] The ability to pattern block copolymers at different length scales, such as from nano- to micrometer-scale, is crucial for a variety of applications, and in a few cases has been commercialized, for the fabrication of devices. Areas include tissue engineering, cell biology, medical science, magnetic storage, semiconductors, and optical devices.[2,3] A variety of patterning techniques have been developed thus far; examples of nanofabrication protocols include graphoepitaxy,[4] direct writing techniques (e.g. dip pen lithography)[5] and photolithography.[6] Among these fabrication methods, photolithography is the predominant technique used for the fabrication of complex devices, regrettably which involves undesirable and harmful substances during the process.[2] The need for cost-effective patterning methods involving environmental friendly protocols remains an open area for exploration.[3] In this context, the ability of patterning without using photoinitiators or additional etching solvents would offer a remarkable advance to this technology. Deep X-ray lithography is one of the direct patterning techniques using photons, which proposes several interesting features; in fact, it is simple, versatile, feasible and free from curing agents.[7] However, the exposure to high-energy deep X-ray requires a synchrotron radiation facility. Alternatively, the use of UV (Ultraviolet) light offers lower costs and accessibility. Unfortunately, the formation of patterns on block copolymer films by UV lithography requires photoactive species, such as

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affinity transition without affecting the integrity of the polymer chain; this effect results in the formation of block copolymer films with a complex architecture of micrometer scale patterns and nanostructures arranged in an ordered fashion (e.g., lamellar, cylinder, cubic). The potential of UV-induced water affinity transition is of particular interest when applied to mesoporous ordered silica thin films, as shown as a preliminary result. In this case the block copolymer plays a double role as it acts a templating[13] and patterning agent at the same time.

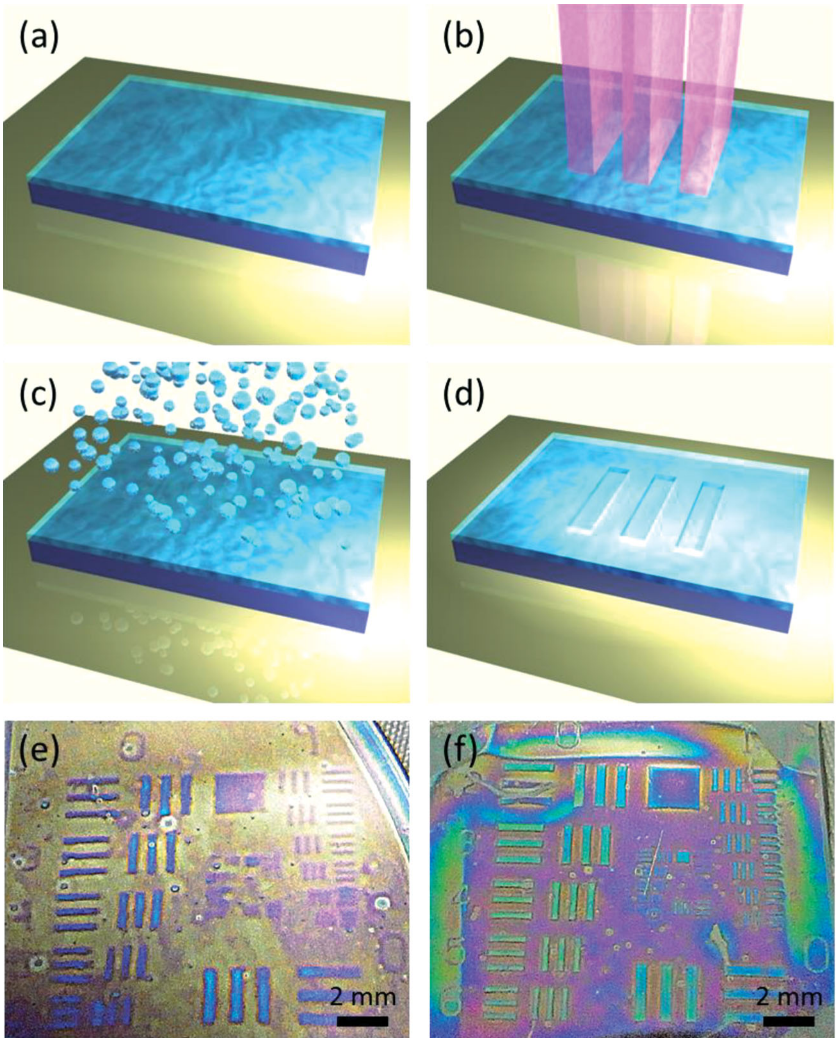

Figure 1. Schematic illustration of the UV lithographic process; (a) a Pluronic film ~200 nm in thickness is deposited on a Si wafer by spin-coating; (b) after deposition the Pluronic film is immediately exposed to UV illumination through a photomask with Cr patterns; (c) subsequently, the film is treated by water vapor; (d) after complete water evaporation, clear patterns appear on Pluronic films. Patterned Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, Mw = 12 600) and F68 ($EO_{80}PO_{30}EO_{80}$, Mw = 8400) films in (e) and (f), respectively.

2. Results and Discussion

2.1. Formation of Patterns on Pluronic Lamellar Films

This novel UV lithography technique requires neither initiator nor polymerizable organic functional groups which are usually inevitable for block copolymer top-down lithography.[8–10] From a technological viewpoint, the proposed technique is simple, inexpensive and versatile; in addition, it is etching process free. This last feature means that neither acids nor organic solvents are used offering an environmental friendly patterning protocol.

The proposed patterning protocol is presented in **Figure 1**. An ethanolic solution of Pluronic was used to spin-coat a thin block copolymer film (200 nm) on a silicon substrate (Figure 1a). The film was exposed to UV illumination through a photo mask with Chromium patterns (Figure 1b); the mask allows for the spatial control of the illuminated regions in the Pluronic film. After UV illumination, no patterns can be visually detected; subsequently the film was treated with water vapor (Figure 1c) for approximately 5 s. The patterns gradually appear whilst the water evaporates from the film (see accompanying video). After complete dryness, the patterns on the Pluronic film are visually evident (Figure 1d).

Figures 1e and f exhibit the versatility of the proposed lithographic technique with alternative Pluronic substances; despite different PPO/PEO ratios and molecular weights, both Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, Mw = 12 600) and Pluronic F68 ($EO_{80}PO_{30}EO_{80}$, Mw = 8400) coatings were precisely patterned with features ranging from several mm down to roughly 100 µm (**Figure 2**a,b). Hereafter, the UV-illuminated part of the film following water vapor treatment is denoted as "UV part", whereas the UV-unilluminated part following water vapor treatment is named "Dark part". All micrometer scale patterns were investigated using stylus type profilometry. Different peak heights were observed; with the Dark parts exceeding the height of the

photoacid generators,[8] UV-curable polymers[9] or polymerized polymers.[10] The requirement of additives has been a drawback limiting versatility of conventional photolithographic processes.

In this article, we report on a novel UV lithographic technique of block copolymer films. The micrometer scale patterns are fabricated on Pluronic films comprised of PEO and PPO segments. Pluronic series (PEO-PPO-PEO) are a family of commercial nonionic triblock copolymers that have been widely used due to their versatility and convenience in a variety of applications.[11] The proposed lithographic approach is based on UV-induced dehydration of Pluronic block copolymer. Although Pluronic has been widely used as UV transparent and resistant material due to its low UV absorbance,[12] it should be noted here that Pluronic is not completely transparent in the near UV region (400–300 nm) as demonstrated experimentally. We found that such a weak absorption is enough to trigger a water

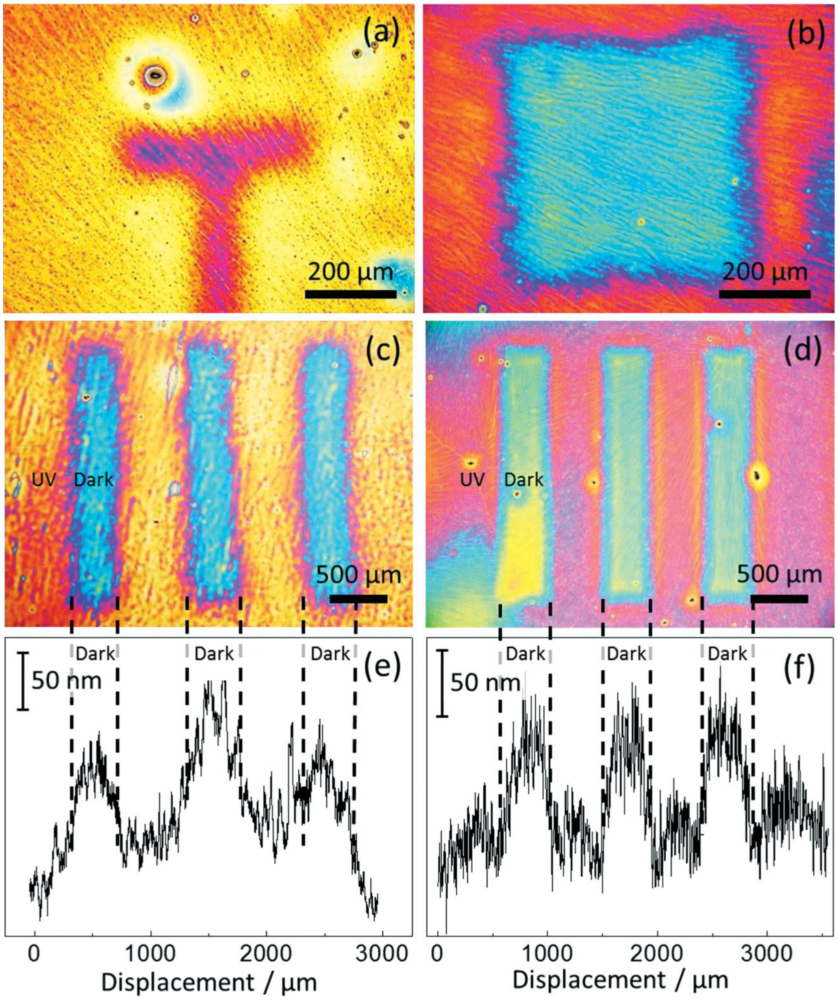

Figure 2. Optical microscope images of a patterned Pluronic film with different patterns (a,b). Optical microscopy image obtained from patterned three line structures in a Pluronic F127 film and corresponding surface roughness (c,e), respectively. Optical microscopy image obtained from patterned three line structures in a Pluronic F68 film and corresponding surface roughness (d,f), respectively.

UV parts, regardless the type of Pluronic used for film deposition, the peak-to-valley amplitude of patterns was ~100 nm (Figures 2c–f). Multiple water vapor treatments can increase the peak-to-valley amplitude to a certain degree. In this study, only single water vapor treatment was performed. Once the Pluronic film has been UV-illuminated and stored in the dark, any post vapor treatment performed within one week induced the pattern formation; this experimental evidence suggests that information towards UV illumination can be recorded on films like a "molecular memory". The obtained micro patterns remain for more than two years in a laboratory environment (temperature: 10 ~30 °C, humidity: 15~60%). However, once the pattern was exposed to high humidity gas stream (>80% RH), the photo/dark contrast decreased gradually.

The crystalline structure of the patterned Pluronic F127 films was studied by X-ray analysis. A profile of grazing-incidence small angle X-ray scattering (GI-SAXS) (**Figure 3**a) revealed the presence of one broad peak at 0.52 nm^{-1} corresponding to a d-spacing of 11.5 nm, which is in agreement with the interlayer distance of F127 lamellae reported in literatures.[14,15] The q_z axis (out-of plane) projection of GI-SAXS profile shown within the red rectangle from Figure 3a is presented in Figure S1. The diffuse scattering appearing at q_z = 0.52 nm^{-1} indicates the existence of the lamellar structure oriented parallel to the substrate.[16] Moreover there is a scattering peak at q_z = 0.95 nm^{-1} which corresponds to the highly ordered peak of the lamellar structure oriented parallel to the substrate. On the other hand, no diffraction peaks were detected at higher angles as shown by wide angle out-of-plane X-ray diffraction (XRD) analysis (See Figure S2). Figure 3b shows the in-plane XRD pattern, where several diffraction peaks were observed and indexed. An intense peak at 19.2° is due to in-plane organization of crystalline PEO chains which are perpendicular to the substrate in lamellar mesophase.[14a,15,17] However, the presence of a broad peak at around 23.4° indicated co-existence of crystalline PEO whose c-axis is not oriented perpendicular to the substrate. Also, a broad halo signal at around 20° can be detected as shown in an inset of Figure 3b, indicating the existence of an amorphous phase. Figure 3c provides a schematic image of the organized PEO segments of basal plane projection. The X-ray characterization defines that the patterned Pluronic film is comprised of crystalline lamellar structures roughly parallel to the substrate. A weak and broad peak detected by SAXS at q_z = 0.52 nm^{-1} with an incident angle of 0° is shown in Figure S2. This indicates a small fraction of lamellar crystallite inclined from parallel to the substrate. A schematic that summarizes the information is presented in Figure 3d where crystalline lamellae embedded in an amorphous Pluronic F127 matrix and micro patterns co-exist in the nanometer and micrometer scale originating a controlled hierarchical structure.

2.2. Pattern Formation Mechanism

Pluronics are considered almost transparent in the UV-visible range,[12] however the absorption spectrum performed on a thin film of Pluronic F127 reveals a presence of a weak absorption signal in the 200–400 nm region (see Figure S2). Although this absorption signal likely triggers the direct pattern formation through UV illumination, the transferred pattern could not be recognized before water vapor treatment; after UV illumination, both thickness and refractive index of UV illuminated and unilluminated regions are identical. Only after the water vapor treatment such parts show distinctive heights.

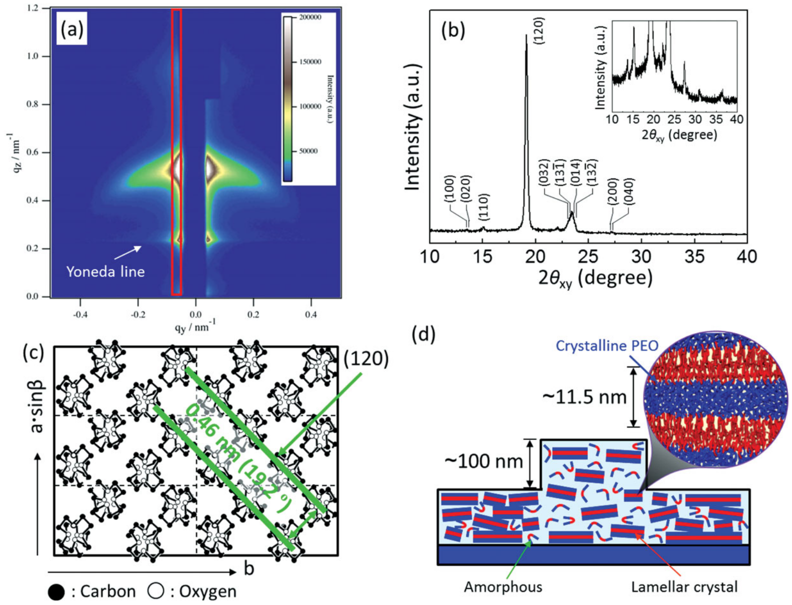

Figure 3. (a) GI-SAXS profile of a Pluronic film. A q_z projection of GI-SAXS intensity within red square part is shown in Figure S3. (b) In-plane XRD pattern of a UV-illuminated Pluronic film. (c) Basal plane projection of a crystalline lamellar structure of Pluronic where PEO chains are closely packed each other.[17] (d) Schematic illustration of a cross-section of patterned Pluronic film with hierarchical structures of nanometer scale lamellae embedded in an amorphous Pluronic F127 matrix and micrometer scale patterns (red: PPO, blue: PEO).

The pattern formation mechanism has been revealed by Fourier Transform Infrared (FTIR) spectroscopy for a film after the UV illumination through a mask with a square pattern; the same region was investigated before (**Figure 4**a) and after exposing the film to the water vapor (Figure 4b). Figure 4c shows FTIR spectra of the UV unilluminated part before and after water vapor treatment. FTIR spectra were collected on exactly the same position, i.e. center of a square pattern. After the water vapor treatment, the peak intensity of the C–H bands (wavelength 2744–3037 cm^{-1}) intensified, indicating an increase of Pluronic molecules in the UV unilluminated part after the pattern formation. From the difference in absorption intensities of FT-IR spectra it is roughly estimated that the amount of Pluronic increases by 1.07 times in the Dark part after the pattern formation. This is almost consistent with the height difference between the parts exposed to UV illumination and the Dark parts, 1.14 (experimental data in Figure S4). This result suggested that Pluronic molecules migrated from UV illuminated to unilluminated parts due to the water vapor treatment. To verify this hypothesis, the UV illuminated part (using opposite pattern of Figure 4b) was investigated using FTIR (Figure S5); a decrease in peak intensity in the same wavenumber region for Pluronic was detected, verifying that a migration effect occurs from UV illuminated to unilluminated parts.

The FTIR analysis has been also used to corroborate the differences between Dark and UV parts in the patterned Pluronic film after water vapor treatment. Figures 4d and e show optical and infrared mapping images obtained from a square pattern (full range spectra are shown in Figure S6). The infrared mapping image was obtained upon integration of the C–H bands in the 2744–3037 cm^{-1} wavelength range; the integrated absorbance is shown in a false color scale. The intensity of the C–H band in the UV part is weaker than the one measured in the Dark part. Assuming that the absorption cross section of the corresponding IR band is the same for both UV and Dark parts, the result indicates that the difference of the height between two parts can be related to the difference in Pluronic masses (i.e.: a larger amount of Pluronic in the Dark part and a smaller in the UV part).

FTIR and ^{1}H NMR analyses were performed before and after UV illumination, indicating that no degradation of Pluronic molecules occurs under UV illumination (Figure S7). These results, in agreement with previous reports,[12] suggest that the degradation of Pluronic can be excluded as a reason for the pattern formation.

A closer investigation of the pattern formation during water evaporation was performed

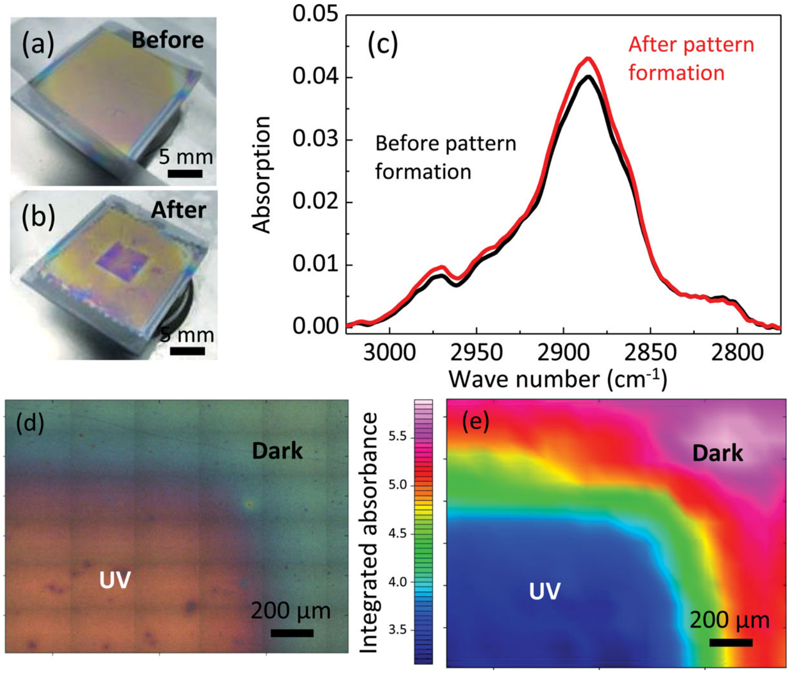

Figure 4. (a,b) Corresponding optical images of before and after formation of a square pattern in same film. The outside of a square pattern was UV-illuminated (UV part), while the inside of a square pattern was UV-unilluminated (dark part). (c) FTIR absorption spectra in unilluminated part before (black line) and after (red line) water vapor treatment. FTIR spectra were corrected on the same position (at the centers of the square patterns in (a) and (b)). (d,e) An optical and the corresponding infrared images obtained from a corner of a patterned square structure in a Pluronic film. The infrared image was obtained upon integration of the C–H bands in a wavenumber region from 2744 to 3037 cm^{-1}; the integrated absorbance is shown in a false color scale. The infrared mapping image provides information about the amount of Pluronic molecules.

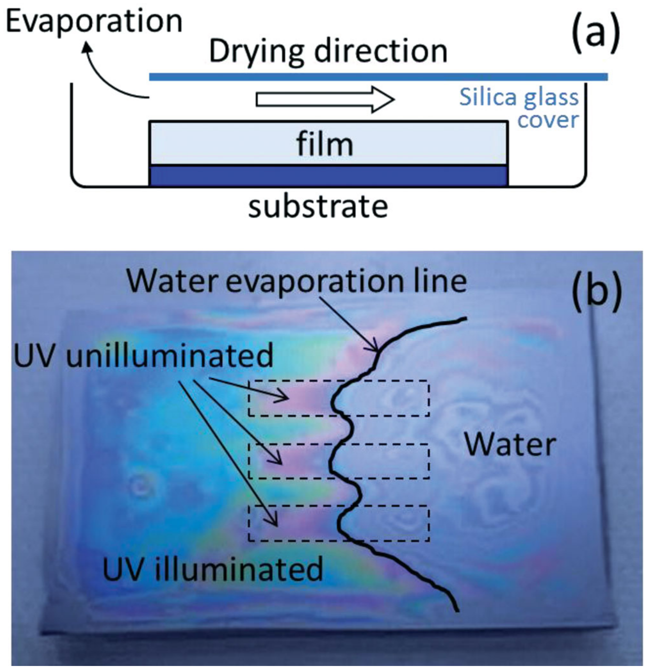

Figure 5. (a) An experimental setup for observation of water evaporation after water vapor treatment and (b) an optical image of the film during drying process (drying direction: left to right). In the optical image, the areas surrounded by dotted lines show the UV unilluminated parts.

using the setup depicted in the schematic of **Figure 5**a; a snapshot of pattern formation process is shown in Figure 5b. The evaporation took place from left to right (see accompanying video); the shape of the evaporation line indicates that the drying rate of the UV illuminated part is faster than that of unilluminated part, which strongly indicates that the water affinity in UV illuminated part is lower than that in the unilluminated part. During the evaporation process, the content of water in the film differs between the two parts, inducing an osmotic pressure at the interface; this osmotic pressure drives the migration of Pluronic molecules from the UV illuminated to unilluminated part. This migration-driven mechanism can explain the obtained pattern in which Dark part is thicker due to the larger amount of Pluronic contained. The present patterning technique is based on migration-induced formation of patterns. The migrated molecules gradually move during water evaporation. Due to migration-induced pattern formation mechanism, the edge of the pattern is not so sharp and the pattern surface is not completely flat. However, optimization of variable parameters, e.g., evaporation speed, film thickness, molecular weight of block copolymer, would improve both the quality and the resolution of patterns.[18]

To further validate the proposed mechanism, we studied the molecular migration promoted by a temperature increase. **Figure 6**a,c show patterns with different size obtained from a Pluronic film heat-treated at 70 °C for 15 min after the UV illumination (no vapor exposure step involved). Surface profile measurements show that the molecular migration was induced only at the vicinity of interface of the two parts with patterns as large as 500 µm (Figure 6b). Under the hypothesis of there being a higher water affinity in the unilluminated part, an osmotic pressure at the interface would occur and the heat-treatment could potentially promote the mobility of Pluronic molecules. As shown in Figure 6a,b, the illuminated part side of 100 µm from the interface was concaved and the unilluminated part swelled in the patterns with 500 µm wide. This short diffusion path is possibly due to the lower mobility of Pluronic molecules at elevated temperatures compared with the case of water vapor treatment. As shown in Figure 6c,d, when the width of patterns is 100 µm or less, the entire unilluminated part thickness increase; this can be explained by the diffusion length at this temperature allowing for the migration along the size of pattern features.

2.3. Effect of UV illumination on Pluronic Molecules

Remarkably, our lithographic method presents a novel process that takes advantage of water affinity differences. The Pluronic

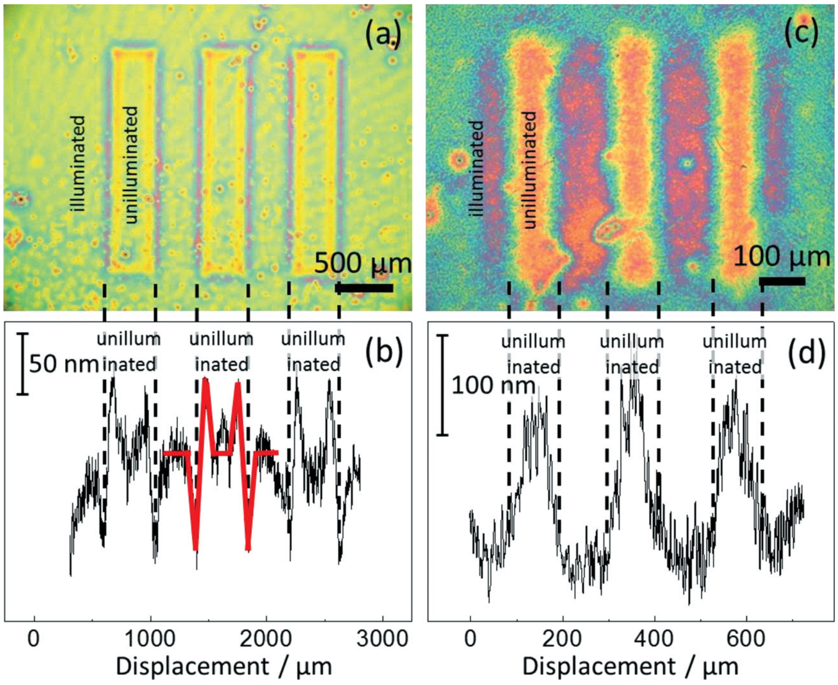

Figure 6. Three lines pattern structures in a Pluronic film prepared by thermal treatment process after space selectively UV exposure. Three line structures with different size ((a) : 500 µm wide, (c) : 100 µm wide) are fabricated on the same Pluronic film. (a) A optical microscopy image of the larger size line with 500 µm wide and the corresponding surface roughness profile (b). (c) A optical microscopy image of smaller one with 100 µm wide and corresponding surface roughness profile (d).

molecules themselves do not involve observable degradation or chemical change because the weak absorption in the 200–400 nm range once excited by 365 nm UV light (see Figure S7). This advantage permits the fabrication of Pluronic films with hierarchal structures of nanometer scale lamellae and micrometer scale patterns. In the macroscopic scale, space selectively UV-illuminated Pluronic films present different water affinities between UV illuminated and unilluminated parts. The UV illuminated parts show the lower water affinity to post water vapor treatment. To understand this phenomenon, we investigated the photo-response of Pluronic coatings as a function of UV exposure. In-plane XRD analyses were performed for UV illuminated and unilluminated parts in an as-illuminated film without water vapor treatment; the comparison of the diffraction patterns indicates that there is no clear difference of the shape and intensity of profiles (See Figure S8). FTIR measurements were performed in both illuminated and unilluminated parts with **Figure 7**a exhibiting three vibrational modes corresponding to C–O–C stretching bands of PEO segments of Pluronic. The mode at ~1114 cm^{-1} presents a weak change in both shape and position (Figure 7b). Peak broadening and a slight shift towards a higher wavenumber were observed for the C–O–C mode after UV illumination. Previous studies assign this peak shift to crystallization from amorphous to crystalline PEO in the Pluronic film.[15] The shift and peak broadening can be also attributed to Pluronic backbone dehydration, as reported by numerous studies.[19] Therefore we argue that UV illumination causes similar effects, i.e. increased crystallization and backbone dehydration in the Pluronic films. X-ray reflectivity (XRR) measurements support this hypothesis because a small increase of film density (See Figure S9) is observed after UV exposure. This result is compatible with an increased crystallinity of the film.

To further investigate the water affinity change induced by UV illumination, in-situ FTIR measurement was performed to monitor in real time the evolution of water evaporation/adsorption in Pluronic powder.[20] The Pluronic F127 powders were mixed with water to cast a thick film of triblock copolymer powders; the film was dried under vacuum overnight followed by rehydration in air for 24 h. A porous thick film of Pluronic powder was produced to investigate the FTIR vibrational bands of the water species; although saturated bands for organic modes were observed, the water mode at 1640 cm^{-1} was clearly detectable. A 4W UV lamp was used to expose the sample and FTIR measurement was utilized to detect the change in water content. During UV illumination a decrease of the water content in Pluronic was clearly observed (Figure 7c). After 60 min illumination, the UV lamp was turned off and the amount of water showed little hydration and plateau thereafter around 90 min. These results show that UV illumination decreases the affinity between Pluronic and water; this strongly supports that dehydration can be triggered by UV illumination. It is important to note that the original water amount was never completely recovered.

The final experiment to prove the water affinity change effect, a water/Pluronic mixture was formed and the aggregation behavior of the amphiphilic polymers in an aqueous solution was examined by a UV-Vis spectroscopic technique in the presence of methyl orange (MO) as a hydrophobic probe molecule. This experiment followed J. Zhang's investigation of Pluronic aggregation in aqueous environments.[21] As shown in **Figure 8**, when the water/Pluronic mixture was exposed to UV light for 5 min, the absorption peak (~455 nm) shifted to shorter wavelengths (~428 nm).[22] Aqueous solutions

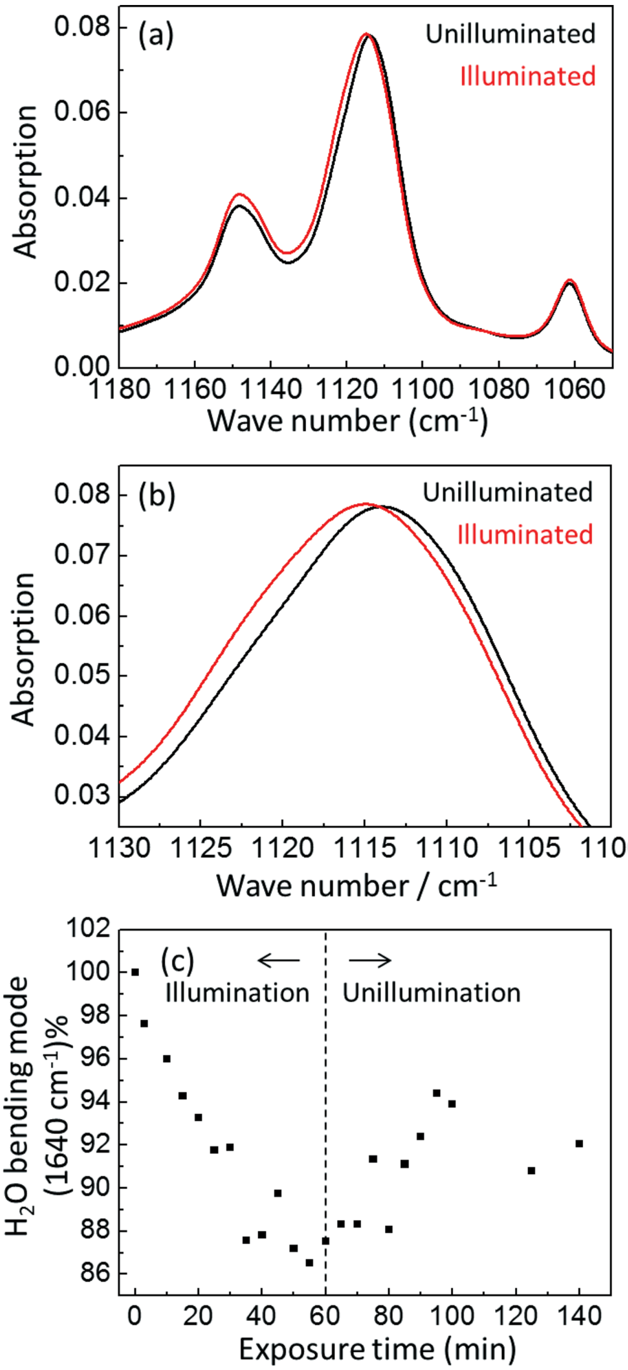

Figure 7. FTIR absorption spectra for UV illuminated (red line) and unilluminated (black line) part of a Pluronic film (before water vapor treatment) in the 1180–1050 cm^{-1} (a) and 1130–1100 cm^{-1} (b). (c) Integrated intensity of the absorption band of water bending mode at 1640 cm^{-1} measured by in-situ FTIR as a function of time for the Pluronic powdery thick film: UV illumination was carried out for 60 min, subsequently the film was stayed still in a dark condition for another 80 min.

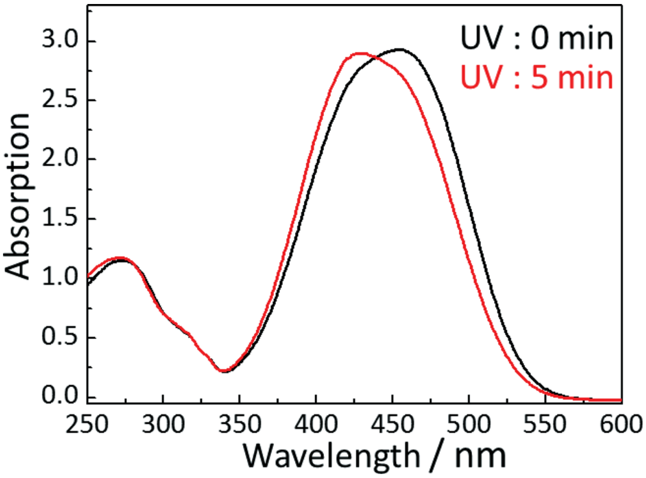

Figure 8. UV-Vis spectra of an aqueous solution of Pluronic F127 containing methyl orange (MO) as a hydrophobic probe molecule; black line: UV-unilluminated, red line: UV illuminated (5 min).

with different Pluronic concentrations were studied without UV illumination; from this experiment we observed that the higher the Pluronic concentration, the more evident the shift to shorter wavelengths (Figure S10). Therefore we can conclude that the UV exposure to Pluronic produces a similar effect of an increasing Pluronic concentration; in fact the water content in the micelles decreases with increasing block-copolymer concentration.[19a] This clearly proves that UV illumination decreases the affinity between Pluronic and water. From the investigation of the effect of UV illumination on Pluronic molecules, even before the formation and observation of geometrical patterns, it was revealed that space-selective UV illumination resulted in a change of crystallinity and dehydration between UV illuminated and UV unilluminated parts in the PEO-PPO-PEO block copolymer film. The simple protocol for the formation of such a physical (crystallinity) and chemical (dehydration) patterns is one advantage of the present method.

To summarize, UV illumination results in a decreased water affinity of Pluronic molecule; a subsequent post water vapor treatment permits the migration-induced formation of patterns due to lower water affinity in UV illuminated part than that in unilluminated part. When block copolymers are used to form self-assembled arrays of micelles, such in the case of mesoporous ordered thin films, the present lithographic method allows to fabricate micrometer scale patterns without using specific photoactive additives. Here we report a preliminary result of patterned mesoporous silica film that takes advantage of the UV-induced dehydration of block copolymer (Figure S11). This is the first report highlighting how Pluronic series play the dual role of structure directing agent for the formation of mesopores and activator for micro pattern fabrication. The overall process is clearly distinguished from previous protocols involving photoacid generators and reactive block copolymers.[23] The change of water affinity in the flare (PEO segments) of micelle of the block copolymer by UV illumination is considered to be responsible for a different aqueous solubility between illuminated and unilluminated parts. Further investigations are ongoing in order to test the versatility of this approach on other mesoporous oxide systems using the present protocols.

3. Conclusion

We established a novel UV lithographic technique for block copolymer film. In the block copolymers, the different water affinities are induced by UV illumination, making possible the fabrication of micrometer scale patterns. This is not restricted to geometrical patterns, with physical (crystallinity) and chemical (dehydration) patterns also being fabricated on the PEO-PPO-PEO block copolymer film. Pluronic molecules themselves do not show degradation or chemical changes, resulting in the block copolymer films with hierarchical structures of nanometer scale lamellae and micrometer scale patterns. In addition, we strongly emphasize that this novel UV lithographic technique requires no initiator and polymerizable organic functional groups which are essential for lithography. By the feature, this UV lithographic technique can be possibly applied to various types of mesoporous inorganic films using Pluronic simultaneously as a templating agent and a UV-activator.

4. Experimental Section

Materials and UV Source: Pluronic F127 (F-127, $EO_{106}PO_{70}EO_{106}$, Mw = 12600) and Pluronic F68 were purchased by BASF and MP Biomedicals, respectively. Ethanol (99.5%) was purchased from Wako Pure Chemical Industries Ltd.. Cleaned Si wafers (100) were employed as a substrate. 500W super high pressure mercury lamp, an interference filter at 365 nm, was employed as a UV source (UV Intensity : 8.6 mW/cm^2).

Formation of Patterns on Pluronic Lamellar Film by UV Illumination and Characterization: A coating solution for Pluronic F127 and Pluronic F68 was prepared by dissolving 0.3 g of block copolymer in 9 mL of ethanol under vigorous stirring. The coating solution was deposited on a Si wafer by spin coating at 1000 rpm for 120 s, and subsequently, at 1500 rpm for 5 s. The block copolymer film on Si substrate was exposed to UV illumination for 45 min through a photo mask with Cr patterns (Edmund Optics). The substrate temperature was kept at 25 °C during the UV illumination. Then, the film surface was directly exposed to humidity (water vapor treatment) produced by an ultrasonic humidifier for around 5 s and slowly dried. In the formation of patterns by heating, UV-illuminated Pluronic film though a mask was placed in a 70 °C oven for 15 min instead of water vapor treatment. The surface roughness of the patterned films were measured by stylus type surface roughness tester (Dektak150). The patterned films were observed using an optical microscope (BX51, OLYMPUS Corp.). Crystal phases of the obtained films were identified by in-plane and out-of plane X-ray diffraction (XRD; SmartLab, Rigaku, Japan) using CuKa radiation (λ = 0.154 nm) and grazing incidence small angle X-ray scattering (GISAXS performed at SPring-8, Japan) and all data were collected at room temperature. Measurement geometry of GI-SAXS is schematically shown in Figure S12. Infrared image was obtained using a Bruker Hyperion 3000 microscope attached to a Bruker Vertex70 interferometer working in the mid-IR range with a conventional Globar source and a KBr beam splitter.

The experiment to investigate a migration of Pluronic using the formation of square pattern was performed using the following process. As-deposited Pluronic F127 film on a Si wafer was exposed to UV illumination for 45 min through a photomask with a square pattern (5 mm × 5 mm) where-by UV light pass outside of a square. At this point, the pattern could no longer be recognized by the naked eyes. A center of an unexposed part was measured by Fourier transform infrared spectroscopy (FTIR: ALPHA FTIR spectrometer, Bruker Optik GmbH). Subsequently, the film was treated with water vapor. A square pattern gradually appeared with the evaporation of water. After complete water evaporation, center of a clear square pattern, which is the exact same position prior to water vapor treatment, was measured by FTIR.

Investigation of UV-Illuminated Effect on Pluronic Molecules: For FTIR measurement, a half of as-prepared Pluronic film was exposed to UV illumination through a mask for 45 min. Both UV and Dark parts on a film were measured by FTIR. An in-situ FTIR measurement was performed on the powder Pluronic material. 0.1 g Pluronic F127 powder was laid on Si wafer and then 100 µL water was deposited on the powder. Then the wet powder on Si wafer was dried under vacuum overnight and left in air to recover the moisture from the atmosphere for 24 hours. The Pluronic powder was measured by time-resolved FTIR with UV illumination (λ = 365 nm, 4W UV lamp was used) for 60 min. After UV illumination for 60 min, UV lamp was turned off and, continuously, the powder was measured by time-resolved FTIR. Aggregation behavior of Pluronic in an aqueous solution was examined by a UV-Vis spectroscopic technique in the presence of methyl orange (MO). 0.3 g Pluronic F127 was dissolved in 9 mL water containing 0.4 mg MO. Then the solution was exposed to UV illumination for 5 min. Ultraviolet-visible spectroscopy (UV-Vis: V-670 spectrophotometer, JASCO Corp.) was performed before and after UV illumination.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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