Photochemical Reactions for Replicating and Aligning Block Copolymer Thin Film Patterns

Dustin W. Janes,¹ Takejiro Inoue,²,³ Bradley D. McCoy,¹ Ishita Madan,¹ Paul F. Nealey,² C. Grant Willson,¹,⁴ Christopher J. Ellison¹*

¹ McKetta Department of Chemical Engineering, The University of Texas at Austin, 200 E. Dean Keeton Stop C0400 Austin, TX 78712 USA
* ellison@che.utexas.edu
² Institute for Molecular Engineering, The University of Chicago, 5801 South Ellis Avenue, Chicago, Illinois 60637 USA
³ Electronic and Imaging Material Research Laboratories, Toray Industries, Inc. 1-2, Sonoyama 3-chome, Otsu, Shiga 520-0842 Japan
⁴ Department of Chemistry, The University of Texas at Austin, 105 E. 24th St. Stop A5300 Austin, TX 78712 USA

A photochemical process for transfer printing patterns formed by block copolymer thin films is described here. An unpatterned, transparent substrate coated in liquid conformal layer is pressed to an epitaxially aligned block copolymer thin film. Irradiation through the sample stack by UV light drives a benzophenone-mediated grafting reaction which covalently bonds the top surface of the block copolymer film to the photopolymerized conformal layer. Separation of the sample stack recovers the original guiding pattern as well as a new chemically patterned substrate replicated from the original pattern. Using a single lithographically directed chemical pattern, 10 replicas are generated, each possessing 28 nm periodicity, perpendicularly oriented microdomains, and long-range epitaxial alignment.

Keywords: block copolymer, benzophenone, transfer printing, directed self-assembly

1. Introduction

Block copolymers (BCPs) are envisioned as next-generation materials for sub-10nm lithography that could complement other patterning techniques.[1] BCPs microphase-separate into periodic microstructures which are considerably smaller than the functional elements in existing microelectronics and hard-disk devices. BCPs are especially attractive as patterning materials when one compares their cost to those associated with next-generation top-down techniques; the price of individual tools for extreme ultraviolet lithography will exceed ¥12 B.[2] Unfortunately, chemical and/or physical guiding patterns are required to direct self-assembly of BP microdomains towards device-oriented structures.[3] For this reason alternative patterning techniques based on the directed self-assembly (DSA) of BCPs may always be intrinsically linked to the top-down techniques necessary to fabricate those guiding patterns.[4]

We think that duplication steps based on transfer printing processes could address this problem by lessening the frequency at which relatively slow and/or expensive top-down techniques are employed.[5-7] Replicas of original BCP patterns can be fabricated by transferring polymer to unpatterned substrates while they are in close, conformal contact. This work describes our efforts to transfer print BCP patterns using applied light energy that activates covalent bonds between the replica substrate and BCP. A liquid, photopolymerizable conformal layer is employed so that the pattern is replicated continuously and over large areas.[5] It is demonstrated here that lithographically directed chemical nanopatterns can be used in 10 successive transfer printing cycles to generate replica patterns possessing defect-free regions that are at least 1 μm × 1 μm.

While the BCP used here is symmetric poly(styrene-b-methyl methacrylate) (PS-PMMA) as small as 10 nm half-pitch, it is anticipated that this concept could be applied to new materials which form even smaller features.

2. Experimental
Unless described otherwise, all materials and methods used here are identical to those described elsewhere.[5]

2.1 Materials

Chemically patterned substrates used in this work were fabricated at the 300 mm DSA pilot line at IMEC in Leuven, Belgium.[8, 9] They possess 3X density multiplication for 14 nm half-pitch PS-PMMA, meaning the feature density of the PS-PMMA pattern is triple that of the chemical guiding pattern.[10] Lamella-forming PS-PMMA with a microdomain periodicity (i.e. full-pitch) of \(L_0 = 28\) nm or \(L_0 = 20\) nm was provided by AZ Electronic Materials (PME-312 Coating 35) or purchased from Polymer Source, Inc. (Mw = 18,500-18,000 g/mol), respectively. A surface-grafted polymer that enabled perpendicular orientation of microdomains at the free surface of a 323 nm thick film of symmetric PS-PMMA (\(L_0 = 20\) nm) was synthesized by free-radical copolymerization of styrene, methyl methacrylate, and hydroxyl ethyl methacrylate (61/38/1 monomer mole ratio in feed).[11] The PMMA cylinder-forming PS-PMMA was described previously.[12] A crosslinkable surface treatment that enabled perpendicular orientation of its microdomains at the free surface of a 600 nm thick film was synthesized by free-radical copolymerization of ethyl methacrylate, methyl methacrylate, and glycidyl methacrylate (94/5/1 monomer mole ratio in feed).

2.2 Transfer Printing Conditions

The conformal layer materials used in this work are composed of 69.5 wt.% dipentaerythritol pentaacrylate (Sartomer), 30 wt. % 4-benzoylphenyl methacrylate, and 0.5 wt. % bis(2,4,6-trimethylbenzoyl) phenylphosphine oxide (BASF). They were mixed in acetone solution and a few drops were applied to cleaned, methacrylate-functionalized glass slides.[5] The acetone was removed by vacuum (< 50 mTorr). The glass slide, now coated in conformal material, was clamped to a silicon wafer supported PS-PMMA film and exposed to UV light. After exposure, the sample stack was separated in toluene at room temperature. 5 sequential toluene rinses were applied to each substrate, while it rotated on a spin coater, to remove unbound polymer.

2.2.1 Exposure Conditions

A Novacure 2100 (EXFO, Inc.) spot cure system fitted with a collimator at the tip of the light guide was used in the transfer printing experiments. It contained an internal \(\lambda = 250-450\) nm bandpass filter, and an external \(\lambda = 300\) nm longpass filter (Edmunds Optics) was placed between the collimator and sample. These filters were used to screen UV wavelengths strongly absorbed by PS-PMMA and to screen visible and IR light that heats the sample. The exposure intensity using these filters and a collimator-to-sample exposure distance of 2 cm was 600 mW/cm² as measured by a thermopile (Coherent, Inc.).

2.3 Self-Assembly Conditions

2.3.1 Self-Assembly of Thin PS-PMMA Films

Thin films of symmetric PS-PMMA (\(L_0 = 28\) nm) were spin-coated onto substrates possessing chemical nanopatterns from the as-received propylene glycol monomethyl ether acetate solution at 2000 RPM. Thin films of lamella-forming PS-PMMA (\(L_0 = 20\) nm) and cylinder-forming PS-PMMA (\(L_0 = 34\) nm) were spin coated from cyclopentanone solution using conditions that yielded a dry film thickness equal to its \(L_0\) on a flat Si wafer. Thin film thicknesses were adjusted by controlling solution concentration and spin coating speed, and were measured by spectroscopic ellipsometry (J. A. Woollam Co., Inc.). The BCP films were annealed for 1h on a 210 °C hotplate held under vacuum to facilitate self-assembly.

2.3.2. Self-Assembly of Thick PS-PMMA Films

The surface treatment for orienting thick films of lamella-forming PS-PMMA (\(L_0 = 20\) nm) was applied by spin coating a ~300 nm thick film from cyclopentanone solution onto a piranha-cleaned Si wafer. The surface treatment for orienting PMMA cylinder forming PS-PMMA was applied by spin coating a 12 nm thick film from 0.3 wt.% cyclopentanone solution at 1500 RPM onto an isopropyl alcohol rinsed Si wafer. Both surface treatments are immobilized onto the wafers by annealing them on a hotplate held at 165 °C under vacuum for 48h. Unbound polymer was rinsed from the wafer by applying tetrahydrofuran to its surface 5 times sequentially while rotating it on a spin coater. Then the wafers were dried with isopropyl alcohol and filtered compressed air. As measured by spectroscopic ellipsometry, the final thicknesses of the surface treatments were 6-8 nm. PS-PMMA was spin coated onto them from cyclopentanone solution. The microdomains of the 323 nm thick lamella-forming PS-PMMA (\(L_0 = 20\) nm) film were oriented perpendicularly at the film’s top surface by annealing the sample for 24h.
on a 210 °C hotplate held under vacuum. The microdomains of the 600 nm thick PMMA cylinder-forming PS-PMMA film were oriented perpendicularly at the film’s top surface by annealing the sample for 24h on a 230 °C hotplate held in an argon gas environment.

2.4 Fourier Transform Infrared Spectroscopy

A roughly ~1 μm thick layer of conformal layer materials was spread onto a double-side polished silicon wafer and affixed to a sample holder so that identical film areas could be exposed to UV light and analyzed by transmission Fourier transform infrared spectroscopy (FTIR). 32 scans with a resolution of 4 cm⁻¹ were averaged. The area under the absorption peak characteristic of benzophenone (C=O, 1660 cm⁻¹) was measured. The converted fraction of benzophenone groups was calculated from

\[
\text{Converted Fraction} = 1 - \frac{A_t}{A_0},
\]

where \(A_0\) is the area under the benzophenone peak for unexposed conformal material, and \(A_t\) is the area under the benzophenone peak after a cumulative exposure time.

3. Results and Discussion

3.1 Conformal Layer Photochemistry Sets Exposure Time

Figure 1. The photochemical grafting reaction is comprised of hydrogen abstraction from BCP by triplet-excited benzophenone followed by propagation of the BCP-centered free radicals to residual acrylate groups in the conformal layer (yellow).

Benzophenone is a classic polymer photosensitizer, and it or its derivatives have been used to initiate polymerizations from polymer surfaces since at least 1957.[13-16] The mechanism of surface grafting in the context of our experiments is shown in Figure 1.[5] The conformal layer materials in contact with the PS-PMMA film are crosslinked by UV light, producing a network with pendant benzophenone and acrylate groups. Benzophenone is excited to the triplet state by further UV exposure and abstracts hydrogen from both PS and PMMA blocks, creating free-radicals at the abstraction site and benzophenone. Propagation of the free-radicals present in PS-PMMA to the residual acrylate groups forms covalent bonds between the top surface of the PS-PMMA film and the conformal layer. Benzophenone and its derivatives can also be used to crosslink a polymer film[17, 18] or anchor polymers to an inorganic substrate,[19] but these reactions are driven by a radical-radical recombination mechanism.

Previous work indicated that the best replication of PS-PMMA fingerprint patterns possessing \(L_0 = 42\) nm was achieved at doses that photo-lysed nearly all benzophenone ketones present in the conformal layer (first step in Figure 1).[5] In order to guide the transfer printing experiments here, the photochemical conversion of benzophenone in the conformal materials at varying exposure time was measured by FTIR. As shown in Figure 2, the fractional conversion of benzophenone increases monotonically with exposure time. Photolysis of about 99% of the benzophenone groups is achieved with 175 minutes of photoexposure, so this exposure time was used in the transfer printing experiments. Because the benzophenone content in the conformal layer is twice that used previously,[5] and because this work employs a λ = 300 nm longpass filter, a 3-fold longer exposure time is necessary.

3.2 Replicating DSA Patterns

Figure 3 shows a schematic of the process used to replicate PS-PMMA DSA patterns. A block copolymer “master” pattern possessing 3X DSA density multiplication is clamped to a blank glass slide coated in liquid conformal material. Light exposure crosslinks the conformal material and drives a grafting reaction between the solid conformal layer and glassy PS-PMMA. Since the transfer printing reaction occurs in the solid state no possibility exists for the PS-PMMA pattern to rearrange. The samples are separated by soaking the sample stack in toluene, which dissolves ungrafted PS-PMMA. The glass slide possesses a
top layer of grafted PS-PMMA, and the guiding pattern is still present on the original master substrate. These samples are coated by a new PS-PMMA layer and thermally annealed to generate a “replica” possessing 1X DSA and to regenerate the master pattern for use in more replication cycles.

Top-down SEM micrographs of samples prepared after the 1st and 10th cycles of the photochemical transfer-printing process are shown in Figure 4. In both sets, 14 nm wide half-pitch chemical patterns have been transferred to the blank replica substrate without erasing the original guiding pattern. Note that every third PS stripe on the master pattern is slightly brighter because of contrast arising from the 3X density multiplication of the original guiding pattern. In contrast, the PS stripes on the replica samples are equally bright because the process has imparted a 1:1 chemical pattern to them. These images clearly demonstrate that duplication cycles can be performed successively using the same starting pattern to generate replica samples possessing high resolution and fidelity.

3.2.1 Defects

Unfortunately, defects are present on the samples after multiple replication cycles have been performed with the same master pattern. For this reason, the micrographs taken for the 10th cycle cannot be described as representative. Generally, more than 10 SEM micrographs at 80,000X magnification needed to be acquired in order to select defect-free regions as shown in Figure 4. Most of the defects appear like those shown in Figure 5: regions in which alignment of lamella is not present and regions in which no vertically oriented lamella can be observed at the film surface. Similar defect structures are present on the replica samples.
At present we can only speculate about the root cause of the defects. Note that none of the experiments in this work have been performed in a clean room environment and mechanical abrasions caused by particulates trapped between the samples are at least partially responsible for defects. Also, no effort was made to filter gel particles.[20] Transfer printing experiments employing much shorter exposure time have been performed and defects are still generated on the recovered master pattern, suggesting that photochemical degradation of the guiding pattern is not responsible. Furthermore, the exposure wavelengths were filtered to avoid this. It is possible that toluene exerts stress on the guiding pattern during the separation and rinse steps. This is supported qualitatively by the features in the guiding pattern appearing dilated after 10 successive transfer printing cycles. If this is the case, defects imparted by the transfer printing process should be reduced by using a different rinse solvent and/or a more stable guiding pattern.

3.2.2 Transfer Printing From Replicas

An advantage of transfer printing processes is that replica samples can be used as a “daughter master” to generate a “2nd generation replica” on an Si wafer substrate. The procedure used was identical to that shown in Figure 3, but the transparent daughter master was positioned between the light source and blank substrate. An example of this is shown in Figure 6, which also includes an image of the “3rd generation replica” generated by transfer printing from the 2nd generation replica. This result is important because it shows that replicas possessing 14 nm patterning resolution and epitaxially aligned microdomain morphologies can be fabricated without using any material that ever existed within the confines of a sophisticated photolithography facility.

![2nd Generation Replica and 3rd Generation Replica](image)

Figure 6. 1 μm² SEM images of 2nd and 3rd generation replicas.

3.2.3 Transfer Printing From Other Templates

Other PS-PMMA materials were investigated as potential starting templates for the photochemical transfer printing process. A lamella-forming PS-PMMA ($L_0 = 20$ nm) was tested to determine if higher-resolution materials could be replicated, and a PMMA cylinder-forming PS-PMMA was tested to determine if alternate microdomain morphologies could be replicated. These starting patterns were not directed by an underlying chemical pattern, but were fabricated by utilizing relatively thick films in which PS-PMMA microdomains self-assemble at the film surface into patterns possessing much higher long-range alignment (i.e. “large grains”) than is achievable in very thin films.[21] Otherwise, the transfer printing procedure is identical to that used to prepare the samples in Figure 4.

The results of this effort are shown in Figure 7. The photochemical transfer printing process described here successfully replicated the pattern formed by lamella-forming PS-PMMA with $L_0 = 20$ nm, because the replica pattern possesses uninterrupted, perpendicularly oriented lamellar microstructures with long-range alignment. Unfortunately, the replica of the pattern formed by PMMA cylinder-forming PS-PMMA possesses structural defects in the self-assembled morphology, although the large-grains are transferred successfully. It is possible that optimizing the conformal layer’s composition could improve this result.

![Master and Replica Samples](image)

Figure 7. 1 μm² SEM images of master and replica samples generated from other PS-PMMA materials.

Note that the PS volume fraction is significantly higher for PMMA cylinder-forming PS-PMMA than for lamella-forming PS-PMMA, which could impact the transfer printing results if the grafting mechanism were more effective for the PMMA block than the PS block. Recent
experiments described by Carbone et al.,[18] and Christensen et al.[17] have confirmed that benzophenone-mediated grafting reactions are more efficient for poly(alkyl methacrylates) than for PS. Hydrogen abstraction rates from phenyl rings in PS are relatively slow, and hydrogen abstraction from the PS backbone promotes chain scission.[17, 18] Qualitatively, these observations explain why the photochemical transfer printing process is more successful for a lamella-forming PS-PMMA than for a PMMA cylinder forming PS-PMMA.

4. Conclusions

In this work, classic polymer photochemistry was leveraged to complement state-of-the-art DSA techniques. A single lithographically-defined chemical nanopattern was used in 10 successive photochemical transfer printing cycles to generate replicas of the aligned lamellae present on its surface. These replicas could also be used as masters to generate more nanopatterns. Furthermore, higher resolution PS-PMMA materials could be employed without any modifications to the normal procedure. The switch from 14 nm to 10 nm resolution represents a 28% improvement, a factor which has historically been non-trivial to achieve in a conventional photolithographic process. Challenges remain in decreasing the amount of defects present in the samples after many replication cycles, as well as to demonstrate the feasibility of pattern transfer to the underlying substrate. Nevertheless, we believe conceptually simple transfer printing processes continue to show great promise in addressing some of the major roadblocks inherent to other next-generation lithography technologies.

Acknowledgements

The authors thank Paulina Rincon and Roel Gronheid of the University of Chicago and IMEC for providing chemically patterned substrates for DSA, and AZ Electronic Materials, Sartomer, and BASF for providing materials. SEM was performed at the Microscopy and Imaging Facility of the Institute for Cellular and Molecular Biology at The University of Texas at Austin. Partial financial support for this work was provided by the Robert A. Welch Foundation (No. F-1709), the Norman Hackerman ARP, Nissan Chemical Industries, Ltd., a 3M Nontenured Faculty Grant, the Lam Research corporation, and a DuPont Young Professor Award.

References