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Solution-Cast High-Aspect-Ratio Polymer Structures from Direct-Write Templates

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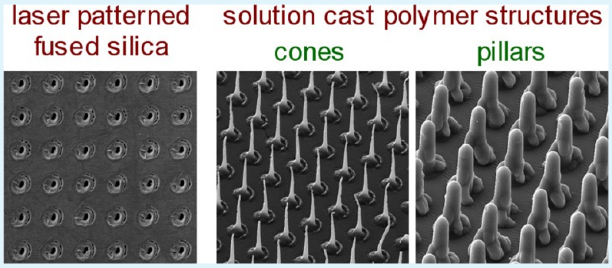
ABSTRACT: This letter presents a novel strategy for template synthesis of polymer structures with laser machined substrates. User-designed patterns of submicrometer holes with aspect ratios >10:1 and depths >10 μm were produced by focusing 160 fs, 5.2 μJ laser pulses on the surface of fused silica with a high numerical aperture microscope objective. Some holes were enlarged by chemical etching. Polymer solutions were cast into the templates to create high-aspect-ratio polymer structures using replication. Engineered polymer structures prepared by this unique method are useful for a number of applications such as high surface area electrodes and biological substrates.



KEYWORDS: *high-aspect-ratio holes, femtosecond laser machining, template synthesis, solution casting, replication, polymer structures*

INTRODUCTION

Template-synthesis is a conventional yet economical method of creating topographical structures, where a patterned surface is used as a mold.[1] In this method, structures are usually obtained from templates by: (i) injecting molten material with the application of heat and pressure; (ii) electrochemical or electroless deposition; (iii) vapor deposition via physical, chemical, or metallorganic vapor deposition techniques; or, (iv) numerous soft lithography techniques.[2−5] Anodized aluminum oxide (AAO), nanochannel glass, track-etched polymers, and lithographically patterned substrates are some of the commonly used molds (also referred to as master pattern in soft lithography) in template-synthesis. AAO templates are prepared by electrochemical oxidation of high purity aluminum films, and have high density of cylindrical and parallel holes, also termed nanopores, arranged in hexagonal-packed arrays.[6] Nanochannel glass (NCG) templates are fabricated by repeated operations of drawing-followed-by-bundling the glass material until the desired hole diameter is obtained.[7] Track-etched polymers are produced by chemical etching of the latent tracks formed in polymer films by bombardment of energetic ions.[8] However, none of these techniques allows complete control on the physical arrangement of the holes produced on the templates even though their diameter and depth can be regulated.[9,10] In comparison, lithography offers ever improving control on the physical arrangement and size of the holes that can be produced.[11]

Photolithography and electron beam lithography are the two most routinely used lithography techniques. Both these template fabrication techniques are primarily based on patterning polymer coated on the substrate followed by reactive ion etching to transfer the pattern into the substrate. Other lithography techniques that have been investigated for patterning substrates are X-ray lithography,[12] ion beam lithography including focused ion beam milling,[13] proton beam writing,[14] and more recently neutral particle lithography.[15] However, these lithography techniques have so far not been reported to produce patterns with high-aspect-ratio (at least 10:1) nano/microscale diameter holes of depths more than 10 μm on large areas at high production rates. Thus, there exists an opportunity to look for alternative lithography techniques that can pattern substrates with user-defined arrangements of high-aspect-ratio (>10:1) holes.[16]

Femtosecond (fs) laser machining is a direct-write lithography technique used to machine transparent substrates like glass for applications such as photonics and microfluidics.[17] White et al. demonstrated that tightly focused single amplified femtosecond laser pulses can produce high-aspect-ratio holes at the surface of fused silica.[18] Holes of aspect ratios as high as 25:1 and depths more than 12 μm were produced by focusing 200 fs laser pulses of wavelength 800 nm through a microscope objective lens of numerical aperture NA = 0.85 onto fused silica. Hole dimensions (diameter and depth) were determined first by cellulose acetate (CA) thin film replication, and then the results of CA thin film replication were validated by imaging the cross-section of the machined hole in a DualBeam FIB/SEM. CA replication of holes results in formation of CA topographical structures that have length-scales comparable to that of the holes, proving that replication or imprinting of high-aspect-ratio holes in fused silica templates is feasible and a novel strategy for creating patterned polymer structures. Moreover, these structures can be subsequently functionalized by coating

Received: September 20, 2012
Accepted: December 17, 2012
Published: December 17, 2012

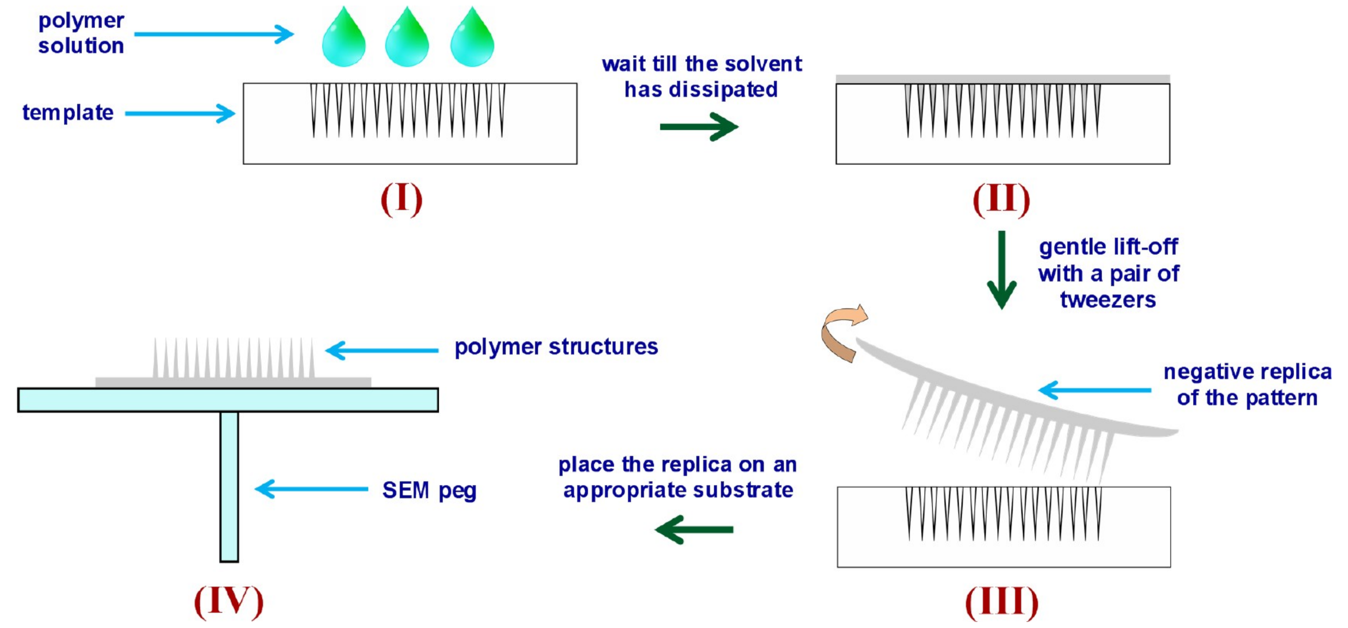


Figure 1. Schematic of the solution casting process used to extract polymer structures from as-machined and chemically etched fused silica templates using replication approach. PE requires an additional step between steps (II) and (III) in which the polymer network resulted from solution casting is heated to and thermally soaked for 2 min at 155 °C, and then slowly cooled in order to form a continuous film before lift-off.

Table 1. Details of the Polymers Used for Solution Casting and the Polymer Structures Created[a]

					as-machined template		etched template	
polymer	source[b]	solvent	wt %	mol wt (× 10^3)	yield	structure length	yield (%)	structure length
PCL	SA	chloroform	2	70–90	0	>30 μm (wires)	100	~13.5 μm micropillars
PCL-8 wt % PEG	VU	chloroform	2	60–70	0	>30 μm (wires)	100	~13.5 μm micropillars
PE	SPI	toluene	10	unknown[d]	100	avg. 8 μm (cones)	100	~13.5 μm micropillars
PMMA[c]	SA	toluene	10	120	100	avg. 9 μm (cones)[f]	100	~13.5 μm micropillars
PVA[c]	AA	DI water	5	57–66	100	avg. 9 μm (cones)	100	~13.5 μm micropillars
PDMS[c]	DCC	heptane	33	NA[e]	50	avg. 7 μm (cones)[f]	100	~12.5 μm micropillars

[a] Yield was determined as percentage of self-supporting polymer structures at 5000× from Figures 3 and 4. The thickness of the final polymer imprint depends on the amount of the solution used initially for casting. Several layers are cast to build up the imprint thickness for convenient handling. [b] SA: Sigma Aldrich; VU: Vanderbilt University; SPI: SPI Supplies; AA: Alfa Aesar; DCC: Dow Corning Corporation. [c] Template coated with antistick layer prior to solution casting. [d] Polyethylene homopolymer (SPI #01090C-AB Positive Replica Powder). [e] Not applicable (Sylgard 184 silicone elastomer kit). [f] Stretched and fallen cones were ignored.

with different types of materials. For example, imprinted CA wires were converted to silica needles by depositing atop a thin layer of silica in a low-temperature chemical vapor deposition process,[19] and silica needles thus produced were used as cell culture substrates for cell differentiation studies using NIH 3T3 mouse embryo fibroblasts.[20] As of yet, only CA thin film imprinting of single-pulse amplified femtosecond laser machined fused silica templates is reported and discussed for practical applications. In this letter, we propose the idea of creating patterned polymer structures from femtosecond laser machined fused silica templates by solution casting in which the diameter of the holes is in the range 750 nm to 2.5 μm and the depth ~15 μm.

■ EXPERIMENTAL PROCEDURE

An amplified femtosecond laser system consisting of a 532 nm continuous wave (CW) diode-pumped frequency doubled laser (Nd:YVO$_4$, Model Verdi-V18 by Coherent, Inc.), a 76 MHz laser oscillator (Model 3941 by Spectra Physics), and a 250 kHz laser amplifier (RegA 9000 by Coherent, Inc.) was used to machine fused silica substrates. The CW laser pumps the oscillator and the amplifier, while the oscillator seeds the amplifier to generate amplified femtosecond laser pulses. The output from the amplifier is a train of pulses with central wavelength 780 nm, temporal length 160 fs, and repetition rate 250 kHz. The Pockels cell within the amplifier allows the emission of single amplified femtosecond laser pulses of energy 5.2 μJ. The laser beam delivered by the amplifier is guided through an assembly of periscopes to the microscope objective lens. The lens focuses the laser beam onto a fused silica substrate mounted on a high resolution nanostage (model ANT95–50-XY nMT by Aerotech, Inc.). The entire femtosecond laser machining system is controlled via a LabVIEW program where user-defined machining patterns are easily designed. Patterns can be machined at the repetition rate of the laser amplifier (i.e., 250 kHz). The motion control system limits the speed at which individual holes can be machined. Currently, with a nanostage velocity of 6 mm s^{-1} and a laser repetition rate of 1.2 kHz, over 4 million holes can be machined at a 5 μm pitch on a 1 cm^2 wafer in less than one hour. Thus, user-defined large area patterns of high-aspect-ratio holes can be machined at high production rates by single-pulse femtosecond laser machining. Further details of the experimental setup can be found in the literature.[21,22]

A 160× microscope objective lens of numerical aperture NA = 1.25 (for water immersion; Leitz Wetzlar Model: ∞/0 PL APO) was used to pattern arrays of holes on a 500 μm thick double side polished fused silica substrate. Machining was done in air without water immersion, so the effective numerical aperture of the lens was less than 1. The as-machined fused silica template was ultrasonically cleaned in acetone and then subjected to polymer solution casting to create polymer structures. A schematic of imprinting by solution casting is shown in Figure 1 and details of the polymer solutions used to make polymer structures are shown in Table 1. The pattern on the template was covered with a few drops of polymer solution (I) and then allowed to dry in normal atmospheric conditions or placed in a vacuum desiccator until the solvent had dissipated and a film was formed on the surface (II). The resulting film is the negative replica of the pattern, the imprint, which consists of structures that form within the holes. The imprint was then slowly peeled-off from the template surface with a pair of tweezers (III) and placed on an appropriate substrate for further analysis (IV) e.g., an aluminum SEM peg or a glass coverslip. In some cases the template was coated with an antistick layer (by vapor deposition of 1H,1H,2H,2H-perfluorodecyltrichlorosilane in a vacuum desiccator) to help release polymer films that stick to the template. Polyethylene (PE) solution does not form film upon solvent dissipation, but a loosely connected network of polymer powder. Thus, to form PE film, the template with the powder network was heated above the melting point of PE at 155 °C on a hot plate and thermally soaked at that temperature for 2 min before turning the hot plate off for a slow cooling. This process successfully forms PE imprints. Once the polymer imprint is peeled from the template, the template can be reused to extract more imprints. The authors have not found a limit to the number of polymer imprints that can be extracted from a single template.

RESULTS AND DISCUSSION

Virtually any polymer that forms a continuous film upon solution casting, with or without the assistance of external energy, can be used to produce high-aspect-ratio patterned polymer structures from these templates. In the current investigation, patterned areas as large as 1.5 cm × 1.5 cm have been successfully solution cast to create polymer structures with high reproducibility and without any observable shrinkage of the polymer film. The morphology of the cast structure depends on the hole morphology produced by single-pulse femtosecond laser ablation, which in turn depends on the spatial profile of the femtosecond laser pulse. Furthermore, the dimensions of the cast structures depend on the dimensions of the holes, i.e., cross-section (both entrance and tip) and depth, which in turn depend on the laser pulse energy used during template fabrication. For a near-Gaussian laser pulse of energy 5.2 μJ, conic submicrometer holes of base diameter 750 nm, tip diameter 150 nm, and depth up to ~12 μm are produced in fused silica templates. By reducing the pulse energy, the depth and the cross-section of the hole can be reduced.[18] To increase the hole dimensions, we can etch the glass template. Hydrofluoric acid (HF) is known to etch fused silica isotropically. Concentrated aqueous solution of potassium hydroxide (KOH) preferentially attacks femtosecond laser affected region in fused silica.[23] The holes can thus be modified by a combination of isotropic etching in HF and a highly selective etching in KOH. Under optimized conditions in both the etchings, the morphology of the holes can be changed from conic to cylindrical. Figure 2 shows scanning electron micrographs of an array of as-machined submicrometer holes (A) and an array of microholes obtained postetching (B). The as-machined submicrometer holes were enlarged by sequential etching, first in HF (Lodyne, BOE, 6:1) for 2 min and then in 10 M KOH at 80 °C for 12 h. The resulting cylindrical holes are ~2.5 μm in diameter (measured at 5 μm depth into the substrate) and up to 15 μm in depth. However, the etched holes appear irregular in shape and larger in diameter at the hole-entrance due to etching of very fine nanocracks that develop near the hole-entrance during femtosecond laser machining.

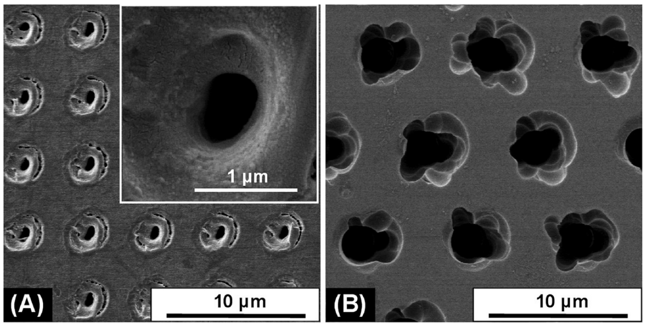


Figure 2. SEM images of two different single-pulse femtosecond laser machined fused silica templates. (A) As-machined femtosecond laser ablated submicrometer holes with average diameter of 750 nm (see inset). (B) Femtosecond laser ablated holes after sequential etching in HF (2 min, Lodyne, BOE, 6:1) followed by KOH (12 h, 10 M KOH solution at 80 °C) with average diameter of 2.5 μm.

SEM images of some of the polymer structures prepared by solution casting are shown in Figures 3 and 4, and only those polymers that are of current research interest are reported here: (A) polycaprolactone (PCL);(B) PCL—polyethylene glycol (PEG) block copolymer; (C) polyethylene (PE); (D) polymethylmethacrylate (PMMA); (E) polyvinyl alcohol (PVA); and (F) polydimethylsiloxane (PDMS). PCL and PCL-PEG structures, Figure 3A, B, appear to be 30−40 μm long wires when extracted from holes with ~12 μm depth. Presumably, these wires undergo stretching during the lift-off process. The adhesive strength between the glass hole and the polymer exceeds the tensile strength of the respective polymers, which results in their stretching during lift-off at room temperature. Because the wires come out very long (>30 μm) due to stretching and are not stiff enough to support their weight, they fall over as irregular-shaped wires. PE, PMMA, and PVA appear as cones with their base diameter around 750 nm and tip diameter in the range 150 to 450 nm as seen in Figure 3C−E. The height and tip diameter of the polymer cones depends on the filling of the hole which is dependent on the interfacial free energy balance between the solution, fused silica, and any trapped vapor. The fact that uniform structures can be formed with dimensions closely matching the hole morphology shows this energy balance is favorable for the wetting of the silica holes by the polymer solutions. PDMS prepared by Sylgard 184 (a silicone elastomer kit by Dow Corning Corporation) is routinely used in soft lithography and microfluidics, and its mechanical properties are tailored by varying the base-to-curer ratio. Although the glass transition temperature (T_g) of PDMS is very low (−125 °C), its 3D cross-linked structure assists the release of PDMS cones from the as-machined holes without breaking or stretching, as shown in Figure 3F. However, most PDMS cones tend to fall over, which may be attributed to low Young's modulus of PDMS (<1 MPa for any base-to-curer ratio). Furthermore, it was observed that most of the erect polymer cones slightly bend in the direction of lift-off whereas some tend to be randomly oriented. The polymer cone yield was found to be very high in all these polymers though some cones break during lift-off in case of PE (Figure 3C) and some tend to stretch near the tip in case of PMMA (Figure 3E). Figure 4 shows SEM images of polymer structures cast from microholes (obtained by etching the template) that appear as micropillars. All the polymers adopt

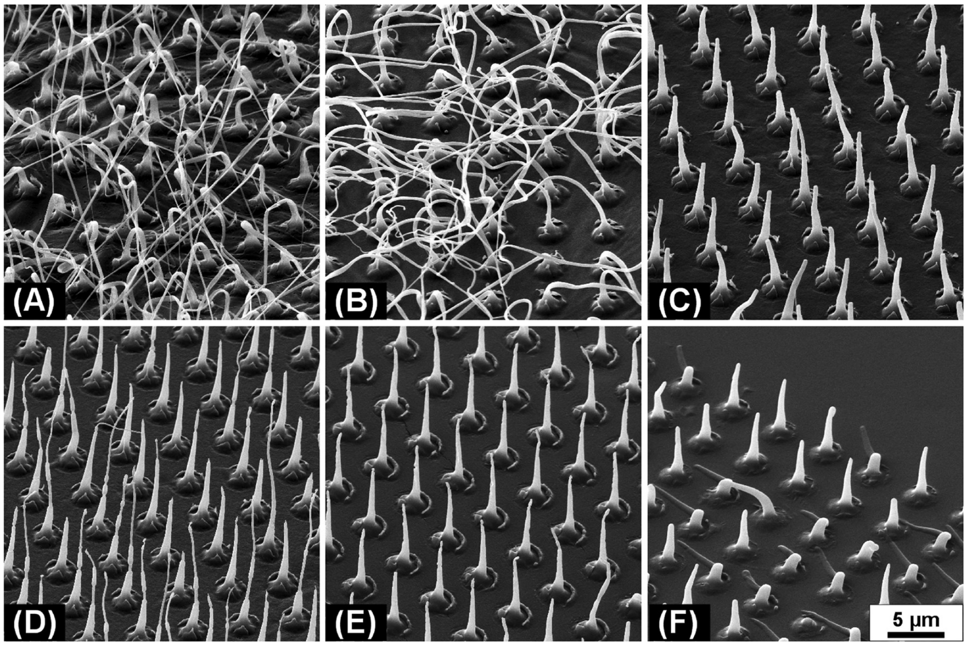


Figure 3. SEM images of polymer structures taken at 45° stage tilt. (A) PCL, (B) PCL-PEG, (C) PE, (D) PMMA, (E) PVA, and (F) PDMS. PCL, PCL-PEG, and PMMA were subjected to vacuum desiccation. PDMS was cured at 80 °C for 2 h.

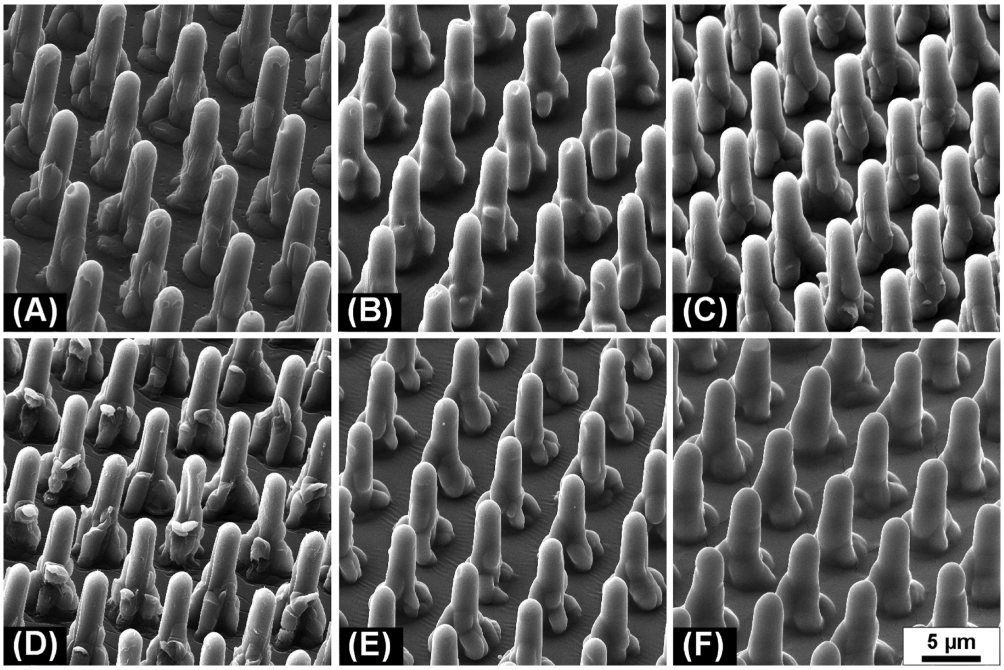


Figure 4. SEM images of polymer micropillars taken at 45° stage tilt. (A) PCL, (B) PCL-PEG, (C) PE, (D) PMMA, (E) PVA, and (F) PDMS. PCL, PCL-PEG, and PMMA were subjected to vacuum desiccation. PDMS was cured at 80 °C for 2 h. PDMS appears enlarged because it was cast from a solution made in heptane, and PDMS is known to swell in the presence of organic solvents.

the shape and dimensions very close to that of the cylindrical holes they are cast from; however, their textures vary because of their physicochemical properties. No stretching, breaking, or bending of pillars was observed and the yield was almost 100% in all these polymers. Besides these polymers, similar observations are recorded for Nafion117, cellulose acetate (CA), polyvinyl chloride (PVC), and Collodion.

In thin film imprinting, the pattern on the template is first wetted by putting a few drops of the solvent (e.g., acetone for CA) and then the polymer film is placed on top of the template. The solvent softens the polymer so that it fills the holes. Once the solvent dissipates, the resulting polymer film forms the negative replica of the pattern; a process quite similar in operation to the aforementioned solution casting. Nevertheless, thin film imprinting is suitable only for those polymers that can be obtained or prepared in the form of thin films and at the same time can be softened by a readily available solvent, thus making it a highly selective process. As a consequence, polymers that do not soften in any solvent cannot be used to prepare topographical structures by thin film imprinting e.g., thermosets like polydimethylsiloxane (PDMS). Blending different polymers or reinforcing polymers with other polymers or nonpolymeric materials leads to the formation of multifunctional polymers with novel properties. Such multifunctional self-supporting polymer structures with varying chemical composition and tunable physical properties can be easily and more efficiently prepared by solution casting. Furthermore, heterogeneous structures can also be prepared by casting multiple layers of different polymers using dilute solutions.

■ CONCLUSION

To conclude, we successfully created high-aspect-ratio (>10:1) patterned polymer structures by combining template-synthesis with solution casting. The templates were fabricated on fused silica by focusing single pulses from an amplified femtosecond laser using a high numerical aperture microscope objective lens, and patterns of high aspect-ratio (>10:1) submicrometer holes of depths more than 10 μm were produced at the surface. Submicrometer holes with conic morphology were converted to microholes with cylindrical morphology by subjecting the template to a chemical etching process. Six polymers of distinct physical properties (PCL, PCL-PEG, PE, PMMA, PVA, and PDMS) were solution cast into the fused silica templates to create polymer structures via replication approach. The solution casting process is highly reproducible and large area polymer structures with high yield and regularity are obtained. This novel-yet-simple strategy for creating high-aspect-ratio patterned polymer structures is currently being explored for applications in biomedical engineering, high-surface-area electrode structures, and photovoltaics.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the Tennessee Higher Education Commission through a grant to the Center for Laser Applications, the University of Tennessee Space Institute, Tullahoma, TN. The authors gratefully acknowledge Dr. George Murray (UTSI) for kindly revising this manuscript during its preparation. We also acknowledge the MIMIC user facility at the Middle Tennessee State University, Murfreesboro for FESEM analysis. PCL-PEG polymer was kindly provided by Dr. Hak-Joon Sung, Vanderbilt University.

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