6-13-2021

Soft Lithographic Replication of High Length-Scale Micropillars From Laser-Ablated Fused-Silica Templates

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SOFT LITHOGRAPHIC REPLICATION OF HIGH LENGTH-SCALE MICROPILLARS FROM LASER-ABLATED FUSED-SILICA TEMPLATES

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AN UNDERGRADUATE HONORS THESIS SUBMITTED IN PARTIAL FULFILLMENT OF REQUIREMENTS FOR THE DEGREE OF

BACHELOR OF SCIENCE

In

UNIVERSITY HONORS & CHEMISTRY

Thesis Adviser:

Shankar Rananavare, PhD

PORTLAND STATE UNIVERSITY 2021

SOFT LITHOGRAPHIC REPLICATION OF HIGH LENGTH-SCALE MICROPILLARS FROM LASER-ABLATED FUSED-SILICA TEMPLATES

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Abstract:

Soft lithography is a well-established route to wafer-scale reproduction of micro- and nanoscale features in a wide variety of materials. Nevertheless, micron length scales have yet to be explored, despite the potential utility of such structures. Here, polymer micropillars of 6-12 µm length, approximately 0.5-1.5 µm wide at 10 µm spacing are reproduced from a polydimethylsiloxane (PDMS) mold made from patterned cellulose acetate (CA). The patterned CA was cast from a rigid fused silica template machined by a pulsed femtosecond laser. Pore topographic features were successfully reproduced in Norland Optical Adhesive (NOA), polycaprolactone (PCL), Nafion, acrylonitrile butadiene styrene (ABS), and CA, with a length scale of 7.7 to 13.5 µm.

Background:

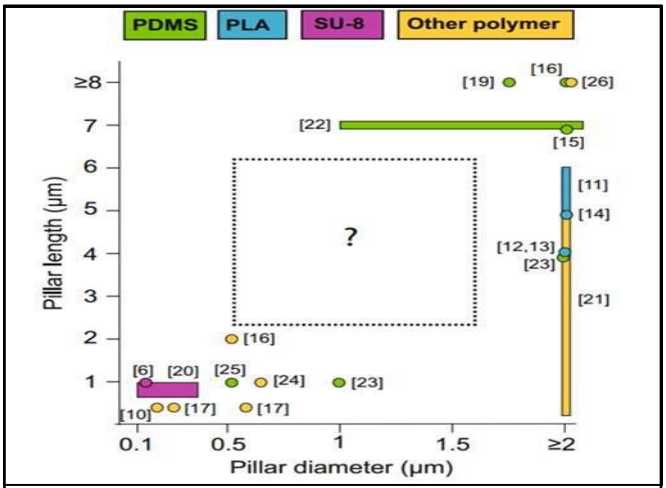

Figure 1: Graphical representation of length scales in literature. The area indicated by a question mark are scales represented in this work.

Soft lithography is a reliable method to fabricate micro- and nanoscale structures in various materials[1]. Yet, the utility of this technique has to be fully realized (Fig. 1). Several length scales have not yet been explored, though there is a need for microstructures of those

dimensions. Specifically, structures with an approximately 1-micron width and ~7 to 15-micron length at 10-micron spacing provide an ideal range for cellular growth scaffolding (Fig. 2). This scale also gives structures the strength to withstand the rigors of circulating fluid in electrochemical processes[2].

Just such structures were produced in 2012 at the University of Tennessee from fused silica templates[3]. To determine the depth of pulsed femtosecond laser ablated holes (Fig. 3), they were filled with cellulose acetate (CA) dissolved in acetone to create a film which was then removed and examined under a SEM[4] (Fig. 4). These 10.5µm-long structures, while not definitively determining the depth of the ablations, were of regular length and topology and

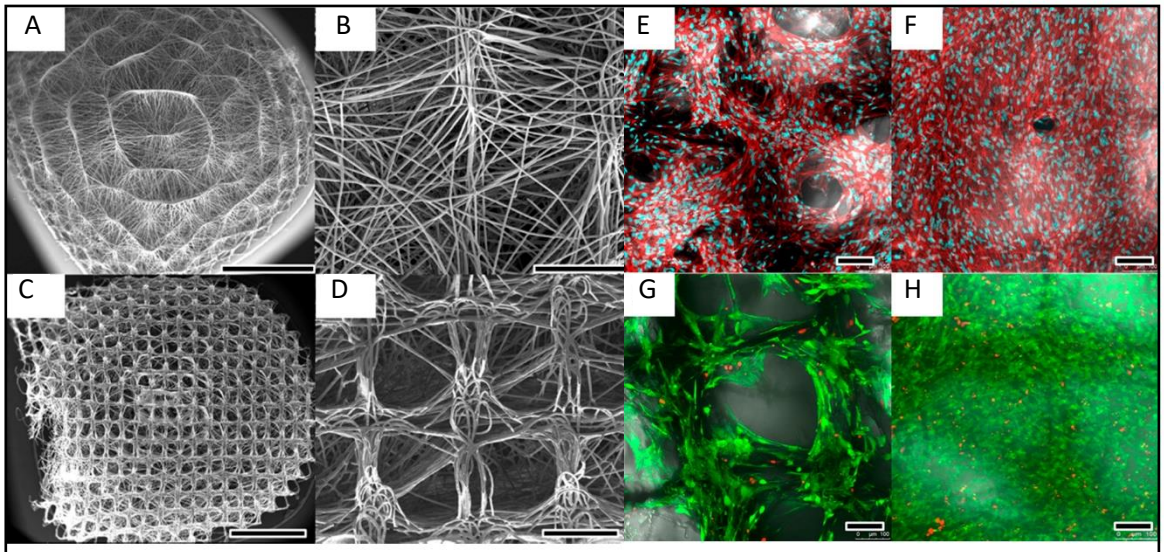

Figure 2: Electrospun PCL fibers in hemispherical geometric arrangement (A-D) populated by living osteoblasts (E, F) then allowed to fully colonize and begin mineralization (G, H).

potentially useful for the applications mentioned above. Focused ion beam (FIB) milling indicated that the ablation depth was at least 11.5 µm (Fig. 5)[5]. Studies have also shown the templates may be sputter-coated without deformation and with SiO_2 using CVD[6,7].

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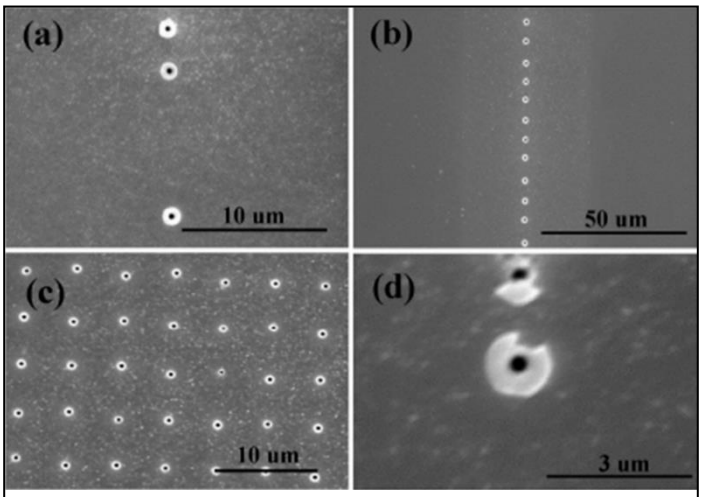

Figure 3: Femtosecond laser-ablated holes in fused silica produced at the University of Tennessee

Given the potential utility of such topology, casting in various polymers was attempted. These templates are small, with a maximum area limited to 2 cm^2 before plasma condensation on the focusing lens begins to defocus the beam, limiting scalability. Substrates are also necessarily planar and, while the film is flexible, creating spheroidal surfaces is impossible. The setup used to create the templates is complex, expensive, requires constant maintenance by highly trained personnel, and takes a long time to set up and run even a single pattern. The ability to duplicate an array of such patterns from these rigid templates in a soft material is desirable.

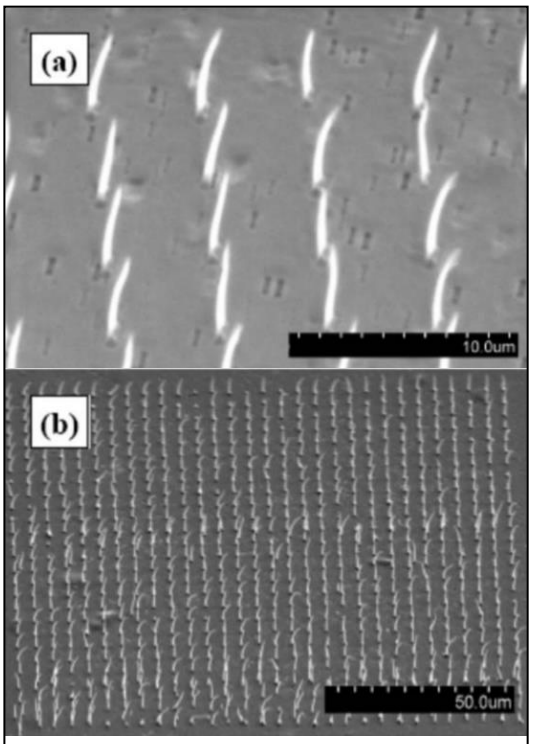

Figure 4: Initial CA casting of a machined fused silica template.

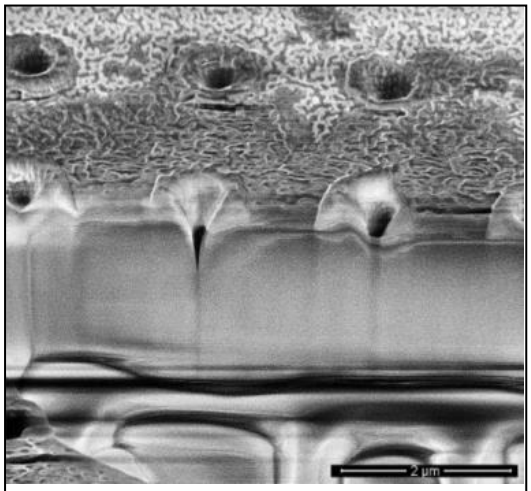

Figure 5: FIB-milled laser-ablation profile in fused-silica[5]

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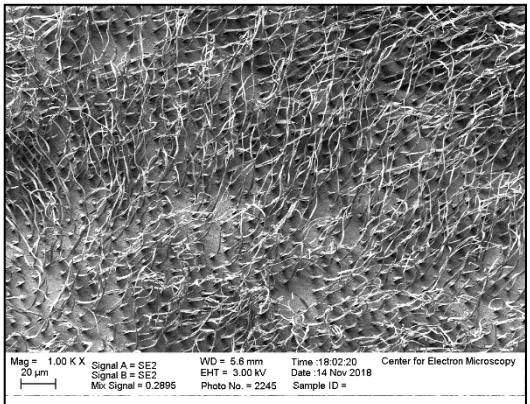

Figure 6: Piliform structures occurring when PCL pattern is removed from hard template

Initial casting attempts by the Tennessee group to produce these patterns in other polymers met with mixed success. Some polymers, such as polycaprolactone, adhered to the inside of the holes, so that the pillars stretched into piliform structures (Fig. 6). Others, such as Nafion and ABS, would not form a film while solvent-casting.

Proposed approach:

My thesis puts forth a hypothesis that low surface energy materials as templating materials may solve this incomplete removal of polymers from the original rigid template. Initial results indicated that when replicated in polydimethylsiloxane (PDMS), these same materials did not suffer from internal adhesion. An alternative approach would be to use an anti-stick coating applied to the templates to alleviate the issue.

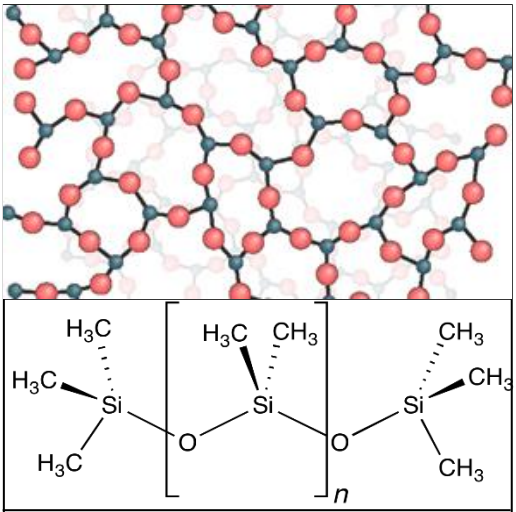

Figure 7: Visual representation of the atomic arrangements of fused silica (top), and PDMS (bottom)[6]

Though both methods use silicon-based materials, the PDMS surface is occupied by methyl groups, while the fused silica surface presents an amorphous network of covalent solid (Fig. 7). The resultant surfaces have different properties as a

result. Two of which most likely to be impactful factors are differences in surface free energy and surface polarization.[8]

The surface energy of PDMS (Sylgard® 184) is approximately 20 mJ/m^2, while that of fused silica is about 100 mJ/m^2. The methylated PDMS has molecular strands that are randomly cross-linked. The methylated surface, along with the relatively small dipole moment of the Si-C bonds, makes the PDMS surface less polar than fused silica, whose Si-O bonds are more polar, uneven on the surface, and may also contain additional cations such as sodium and potassium. Surface polarity differences affect the interaction of both the carrier solvent and the dried polymer with the internal surface of pores.

EXPERIMENTAL:

Fused silica templates were used as received from the University of Tennessee Space Institute. Methyl ethyl ketone, chloroform, acetone, isopropanol, PCL (Mn=80000), CA film, and Nafion were from Sigma Aldrich. Sylgard® 184 PDMS was from Dow, and ABS from BASF.

First, 2% and 5% w/w polymer solutions were mixed in glass vials, capped, and allowed to mix on a stirring plate for 24 hours. Next, hard templates were sonicated in water for 5 minutes, dried, then O_2 plasma treated in a March Plasmod plasma cleaner for 20 minutes. The cleaned and surface treated templates were then placed on a level surface, and a few drops of acetone

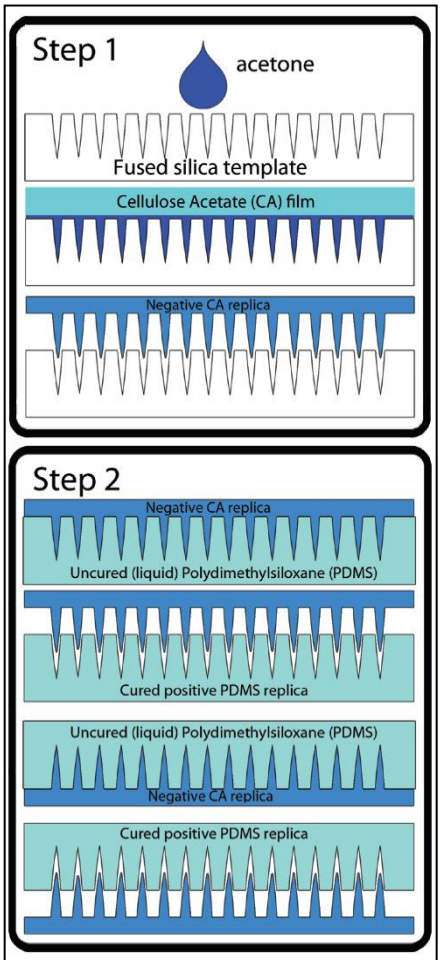

Figure 8: Schematic outlining the initial CA casting protocol, step 1 and PDMS replication Step 2.

were applied. Before acetone evaporates, a piece of CA film was placed on the acetone above the pattern and then allowed to dry for 15 minutes until the solvent evaporated, the polymer appeared fully dry (Fig. 8).

Once dried, the dry CA film was quickly peeled off in a single motion then immediately transferred to a polymer microscope slide cover, using a "peel and stick" SEM adhesive tab. This negative pattern was then either mounted to a stub for characterization or cast in PDMS.

Replicated patterns were placed in the bottom of a small petri dish, where mixed and degassed PDMS was very slowly poured on top of it from the edge of the dish or placed gently on top of mixed PDMS. The PDMS was then kept on a hot plate at 100°C for 4 hours until cured. The initial patterned CA film was then removed and discarded.

Replication was performed by first applying several drops of 2% polymer solution on the PDMS template and observing until nearly dry. Before complete drying, a few drops of the 5% solution were added, and the polymer was allowed to dry. CA replicas from PDMS were performed in the same manner as the initial replicas from the rigid template. The polymer films were then removed from the PDMS and mounted to SEM stubs, gold sputter-coated to a

thickness of 8-15 nm (to prevent substrate charging), then characterized in a Zeiss Sigma SEM and Fiji v1.53J image analysis software. One critical advantage of this approach is larger size patterns (i.e., greater than 2 cm^2) can be generated by adhering multiple negatives to a single surface, then casting in PDMS.

Results & Discussion:

Because the patterned polymer film must be free of contaminants before casting in PDMS, especially metals, as they interfere with the curing catalyst. Polymer pattern cannot be characterized before it is cast and removed from PDMS. This makes a direct measurement of length-scale retention impossible. Similarly, the PDMS casting must be cut out from the block before inserting in the SEM chamber, and its use is very limited once cut out. Due to its transparency, PDMS is not easy to characterize it optically.

Furthermore, the PDMS has a very low surface energy, so it does now wet with many solvents[9]. Similarly, the fused silica templates are also challenging to wet completely. It therefore proved necessary to activate these surfaces before casting. To that end, treating in an O_2 plasma cleaner increased the surface wettability of both fused silica and PDMS templates.

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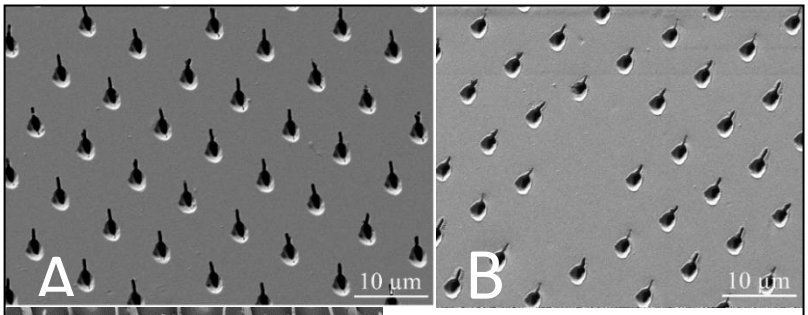

Figure 9: SEM images of the original hard template (A), positive replica in PDMS (B) from CA pattern (C) cast from original quartz template. It is noted that the keyhole shape at the base is preserved.

PDMS behaved as expected, faithfully reproducing patterned templates from the initial CA negatives (Fig. 9). PCL and ABS had difficulty forming cohesive films. But it was found that a two-step application of first a 2% then 5% w/w polymer solution after a 4 to 12-minute variable drying time resulted in a cohesive film. Replication was successful by this method with PCL, ABS, Nafion, NOA, and CA (Fig. 10). The replicated structures from PDMS were 7.7 to 13.5 µm in length (Fig. 11). The differences in the measured pillar lengths, reproduced from the same fused silica template of 11.5 µm pore depth, imply an irreversible stretching (when length > 11.5 µm), breakage (when length < 11.5 µm) during two replication stages (i.e., CA and polymer castings). Other plausible mechanisms include

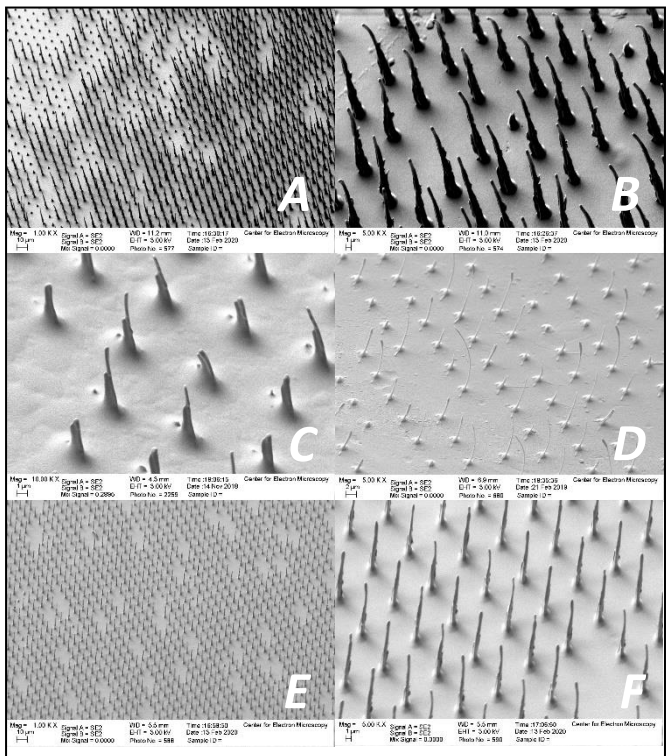

Figure 10: Structures replicated via soft lithography. PCL (A & B), ABS (C), Nafion (D), and NOA (E & F).

incomplete pore filling dues to viscosity and/or atmosphere trapping in the holes, and the dimensional expansion of some cross-linked polymers when curing.

Correlations between the mean length and Young's modulus and tensile strength are apparent, as both NOA (1 GPa) and CA (>1 GPa) have much greater Young's modulus than PCL (350 MPa). A similar trend exists in the tensile strength of these polymers, with PCL exhibiting the lowest values. More detailed modeling studies are needed to establish these correlations.

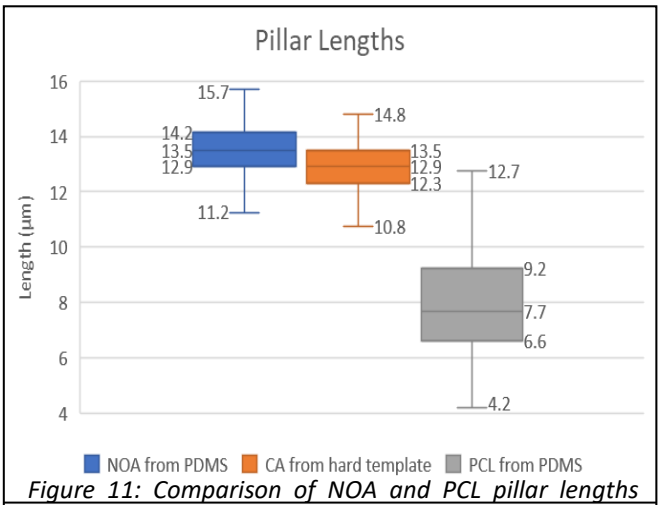

Figure 11: Comparison of NOA and PCL pillar lengths obtained from soft lithographic process with CA pillars obtained from original hard template.

It is possible to increase the dimensions of pillars by exploiting wet etch techniques. Silica walls of pores were etched in 48% HF for 3 minutes at room temperature. Following a similar duplication process, the ABS-cast structures were seen to be malformed in a

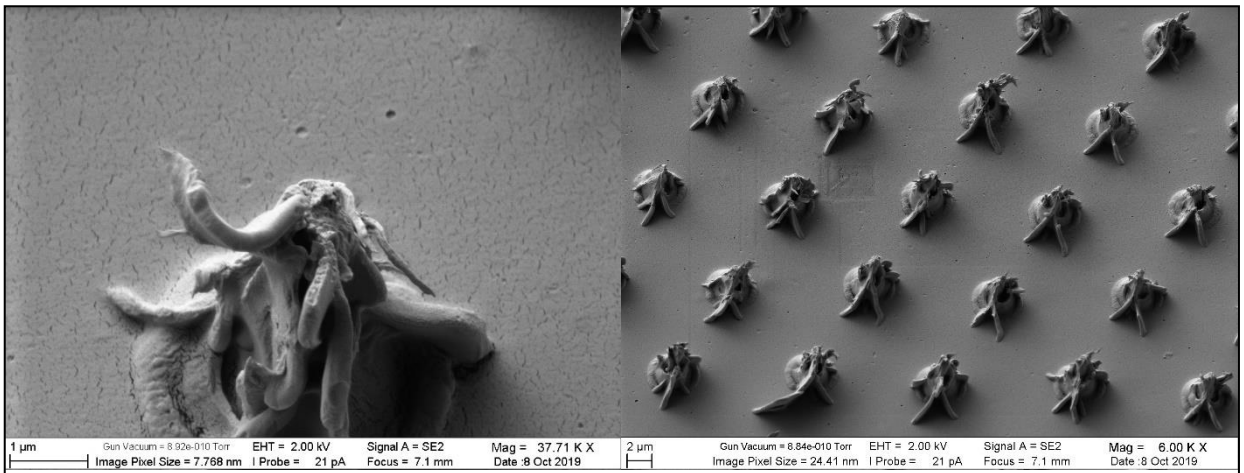

Figure 12: Deformed ABS structures produced by fused-silica template after HF etching.

complex manner but exhibited many repeating, intricate nanoscale features, significantly increasing surface area (Fig. 12).

The observed unique set of topologies is likely reproducible in many more polymers and composites and is inherently compatible with many dopants.

Future work on this project should include such studies deploying polymers, proteins, and macromolecular systems in general. One may envision potential use of the template as a scaffold for membrane tissues and possible surface activation for electrochemical processes and Hall thrusters[10].

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Acknowledgements:

PSU Department of Chemistry

Dr. Shankar Rananavare

Emmanuel O. Abdul

Dr. Deepak Rajput

Cornelia Coleman and Brianna Avery of the Honors College

Dr. Dean Atkinson

University of Tennessee Space Institute

Dr. Leno Costa