UV Embossing of Sub-micrometer Patterns on Biocompatible Polymeric Films Using a Focused Ion Beam Fabricated TiN Mold

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The development of easily accessible and cost-effective large area nanopatterning techniques using biocompatible film is important for gene and drug delivery and tissue engineering.[1−2] It has been shown, for example, by Xu et al.[1] that aligned electrospun nanofibers with diameter of about 500 nm enabled the in vitro human coronary artery smooth muscle cell to align and express a spindle-like contractile phenotype resembling that in our bodies. We are interested in UV nano-embossing with similar dimensions using biocompatible poly(ethylene glycol) diacrylate (PEGDA). PEGDA has been shown to be biocompatible and nonadhesive to protein and cells.[3,4] Others have produced micrometer-sized (not nanosized) poly(ethylene glycol) patterns using contact photolithography, which is restricted to resolution of about 1 μm. Electron beam writing or focused ion beam (FIB) lithography are capable of nanopatterning but typically are serial and time-consuming and require specialized substrates such as silicon wafer or electron beam resist. We used FIB method to fabricate a mold with sub-micrometer features and then used this to replicate multiple silicone rubber molds for UV embossing. The replication of soft rubber molds and UV embossing are quick, convenient, and easily accessible.

FIB has been successfully used by others[5,6] for nanopatterning of silicon and poly(methyl methacrylate) but not titanium nitride (TiN), which has the desired hydrophobicity and chemical and metallurgical stability for durable multiple-use master molds.[7] The water contact angle on TiN has been measured to be 71.2 ± 2.5° compared to 10.5 ± 3.0° for silicon. Soft lithography, that is, the use of silicone rubber for replication, is a well-studied process,[8] although little study focuses on the fouling of the mold by repeated silicone rubber nanomoldings. Hull et al.[9] have used FIB etched PMMA for casting silicone rubber. However, there was no reference to the durability of the PMMA mold. Because of the above-mentioned characteristics, TiN can be expected to be more durable than PMMA. Philips Research[10] has demonstrated sub-micrometer UV imprinting on a rigid silicon substrate. However, UV embossing on a flexible biocompatible substrate without the use of a highly sophisticated nanoimprint machine has not previously been demonstrated.

To create the master mold, a 1-μm-thick TiN film was deposited on a ⟨100⟩ silicon substrate by a reactive dc magnetron sputtering system equipped with a cryogenic pump. The base vacuum pressure was less than 2.0×10^{-7} Torr. The sputtering was conducted with a 3-in.-diameter sintered titanium target (99.99% pure). The depositions were carried out using a 1:1 mixture of Ar and N_2 and monitored using a quartz crystal with 0.01 nm/s accuracy. The applied dc power was 200 W. The substrate temperature was maintained at 500 °C during deposition.

For FIB lithography, a Focused Ion Beam Series 9500EX (Micrion) with a Ga^+ ion source operating at 40 kV and room temperature was used. The beam current was 55 pA and the angle between the beam and the plane of the sample was 90°. The spot size (full width at half maximum) was 15 nm and the dwell time at each point was chosen to be 1 μs. The area of the pattern was 85 μm × 55 μm. The total milling dose and time were approximately 0.65 nC/um^2 and 6 h, respectively. The limit aperture was set at 25 um and the working pressure was 1.7×10^{-7} Torr.

SLYGARD 184 (Dow Corning) silicone was used for replication from the TiN master. For UV embossing, the UV resin comprised 99.7/0.3 (w/w) of PEGDA with a number average molecular weight of 700 (Sigma-Aldrich) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651 from Ciba Chemicals). The UV intensity used was 60 mW/cm^2 and the exposure time was 7 s. Details of rubber casting and UV embossing procedure can be found in ref 11. The mold and replications were examined using a field-emission scanning electron microscope (SEM) (Joel JSM-6700F) and a scanning probe microscope (SPM) (NanoScope IIIa from Digital Instruments).

TiN mold was used for at least 8 rubber castings and the 4th rubber casting was used as the mold for 8 PEGDA embossings. For clarity sake of the generations used, the TiN, rubber, or PEGDA shall be denoted by TiNβ, αRubberβ, or αPEGDA, respectively, where α indicates the αth replication from previous generation

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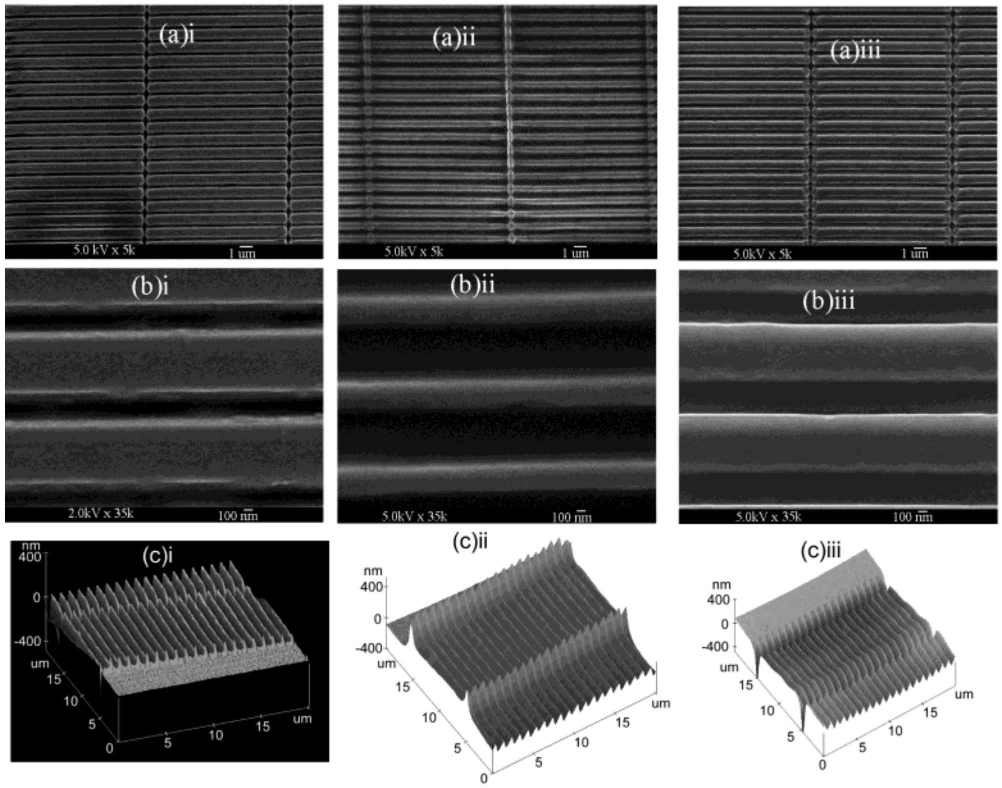

Figure 1. Morphology of (i) TiN0 master, (ii) 1Rubber0, and (iii) 1PEGDA: (a) SEM (low magnification), (b) SEM (high magnification), and (c) 3-D SPM images.

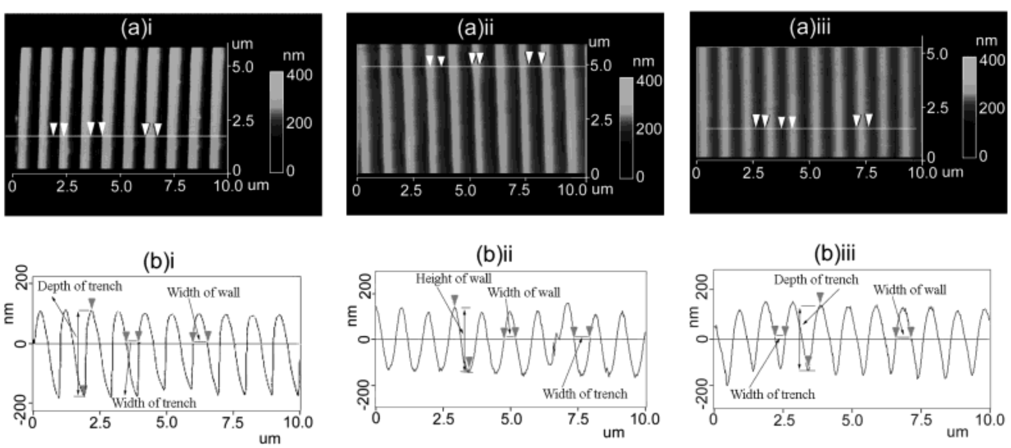

Figure 2. 2D SPM images: (a) plan view and (b) z-profile of (i) TiN0, (ii) 1Rubber0, and (iii) 1PEGDA pattern.

and β the number of replications made from it. A comparison of the SEM and 3-D SPM images (Figure 1) of the original unused TiN, first rubber molding, and first PEGDA molding indicates that the replications were good. There is a remarkable resemblance between TiN0 and the embossed 1PEGDA. Figure 2 is a representative 2-D SPM z-profile. From SPM measurements, the dimensions of TiN0 and all the unused rubber replications (1Rubber0 to 7Rubber0 in Table 1) matched closely. There is little dimensional difference between the different generations of rubber moldings or TiN mold after repeated replications (Table 1). We have found that the TiN mold can be used for more than 20 times without much change in the dimensions of the TiN mold or rubber moldings. This can be attributed to the low surface energies of both the TiN and silicone. The roughness of the TiN0 mold was also measured with SPM and found to be 4.0 ± 2.0 nm, demonstrating that

Table 1. TiN Master and Rubber Mold Dimensions (Each Measurement Is the Average of at Least 10 Data Points)

replication times	height/ depth (nm)	width of wall (nm)	width of trench (nm)	rms roughness (nm)
TiN0	280 ± 7	610 ± 10	390 ± 8	4.0 ± 2.0
TiN8	277 ± 9	605 ± 8	395 ± 11	7.0 ± 2.0
1Rubber0	276 ± 14	396 ± 7	607 ± 11	9.5 ± 3.0
3Rubber0	268 ± 10	401 ± 11	602 ± 8	8.3 ± 5.0
5Rubber0	266 ± 12	398 ± 13	592 ± 15	11.1 ± 7.0
7Rubber0	270 ± 9	400 ± 10	596 ± 9	10.5 ± 7.0

FIB lithography of TiN film produces very smooth surfaces suitable for nanopatterning. SPM analysis shows that the roughness of the TiN master increases only slightly to 7.0 ± 2.0 nm after the eighth rubber replication.

Comparison of the SEM images of 1PEGDA and 8PEGDA (Figures 1 and 3) show that the eighth PEGDA

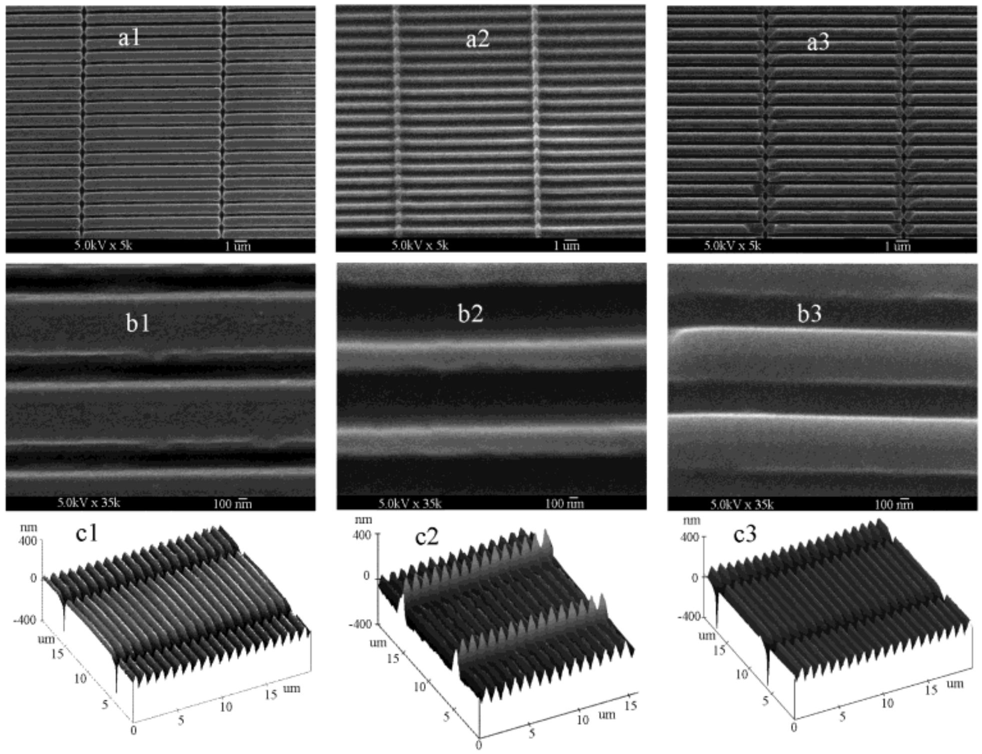

Figure 3. Morphology of (1) TiN8, (2) 8Silicone0, and (3) 8PEGDA: (a) SEM (low magnification), (b) SEM (high magnification), and (c) 3-D SPM images.

Table 2. PEGDA Molding Dimensions (Using Fourth Generation of Rubber Mold) (Each Measurement Is the Average of at Least 10 Data Points)

rubber/ PEGDA	depth/ height (nm)	width of trench (nm)	width of wall (nm)	rms roughness (nm)
4Rubber0	267 ± 11	597 ± 12	400 ± 12	9.7 ± 6.0
PEGDA1	272 ± 11	384 ± 12	620 ± 8	12.3 ± 5.0
PEGDA3	268 ± 8	403 ± 7	598 ± 5	10.6 ± 4.0
PEGDA5	270 ± 13	392 ± 11	605 ± 9	9.6 ± 7.0
PEGDA7	266 ± 10	389 ± 9	609 ± 11	11.2 ± 5.0

molding appears to replicate the major dimensions well (Table 2) but has some minor surface defects. The low PEGDA shrinkage (about 5%) was critical for successful embossing. The surface of silicone rubber or PEGDA can be modified to increase the hydrophobicity to further decrease the surface defects. In addition, Tables 1 and 2 show the maximum root-mean-square roughness of TiN or rubber or PEGDA is lower than 12.3 ± 5 nm, so the surface of these moldings is very smooth.

We have demonstrated faithful replication of sub-micrometer scale 3-D structures on a biocompatible polymer using a simple, accessible technique of UV embossing from a silicone rubber mold replicated from an ion-beam-etched TiN master mold. The replication technique is low cost and does not require special processing conditions. The technique should permit several tens to hundreds of easily UV embossed PEGDA replications from a sub-micrometer patterned TiN master mold.

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