

Additive Fabrication of Multiscale Metasurface by Electrohydrodynamic Nanotexturing of Two-Beam Interference-Patterned Photopolymer Surface

Qiang Li, Inho Cho, Rana Biswas, and Jaeyoun Kim

*Department of Electrical and Computer Engineering, Department of Physics and Astronomy, Department of Civil, Construction, and Environmental Engineering, Microelectronics Research Center, Iowa State University, Ames Laboratory
pleasmon@iastate.edu*

Abstract: Adding nanotextures to polymer surfaces already corrugated by 2-beam interference lithography is highly challenging. Using softlithography, triboelectricity, and electrohydrodynamic lithography, we fabricate multiscale metasurfaces by adding nanovolcanoes to sinusoidally corrugated NOA73 surfaces. © 2019 The Author(s)
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1. Introduction

Adding nanotextures to polymer surfaces that are already patterned by two-beam interference lithography is highly challenging. Since polymer surfaces are compatible with triboelectric charging effect which, in turn, is compatible with nanoscale patterning, their combined use can provide a good approach to achieve such a multiscale patterning. Tribocharging of elastomer surfaces due to their electrical or frictional contact with other materials is attracting substantial interest, with the resulting tribocharges already playing crucial roles in many applications. Recently, a similar tribocharging has also been observed on the surface of the elastomer poly(dimethylsiloxane) (PDMS) as the result of replica molding. Ensuing studies revealed that the level of tribocharging is strong enough to influence some microfluidic functionalities such as channel electrophoresis. So far, however, this replica molding-induced tribocharging phenomenon has been studied only on flat, untextured elastomer surfaces. It is rather ironic since replica molding is the primary method for surface texturing of the PDMS. Questions regarding how those textures affect the tribocharge's generation and distribution patterns and, more importantly, how they can be utilized for nanotexturing of another polymer surface have been left unanswered to date.

2. Approach

Here, we attempt to answer the questions and achieve multiscale optical patterning of NOA73, a well-known UV-curable photopolymer from Norland Product Inc., through a multi-physical investigation employing replica molded PDMS nanostructures. Since the resulting tribocharge distribution is below the range of direct imaging, we adopt indirect approaches which pair experimental techniques, such as scanning Kelvin probe microscopy (SKPM) or electrohydrodynamic lithography (EHDL), with iterative numerical modeling. In addition, we also model the replica molding process from the mechanical point of view. Based on the findings from the investigations, we identify the frictional stress, induced by the demolding action, as the main factor governing the tribocharge's nanoscale distribution pattern. This work also establishes a useful application for the resulting ring-shaped tribocharge by configuring it to enable EHDL to build nanovolcanoes with 10 nm-scale nanocraters, a dimpled 3D nanostructure.

3. Methods and Results

In EHDL, liquid-phase polymer becomes polarized and attracted by spatially modulated electric fields and forms out-of-plane structures upon solidification. Therefore, the gap between the source of the electric field and the polymer surface is one of the most important factors in EHDL. Conventional EHDL utilizes patterned electrode as the source of the electric field and separately prepared dielectric thin film stripes as the spacers. Here, we utilized the tribocharged PDMS nanocups (Fig. 1a) as the source of the electric field. To place a gap between them and the polymer surface, we selected a photopolymer, which undergoes low but definite volume shrinkage upon exposure to UV irradiation, as the EHDL's target material and then textured the surface with a spatially modulated UV beam. The recesses in the resulting texture provide the gaps.

Specifically, we spin-coated NOA73 into a thin film on a Si-substrate, and exposed it to a UV two-beam interference pattern (Fig. 1b). Then the NOA73 surface became sinusoidally textured due to the local volume shrinkage (Fig. 1c). More details on the sinusoidal texturing of NOA73 can be found in Methods. Note that even though the NOA73 thin film's inner volume becomes well cured by the UV exposure, a thin layer at its top surface remains fluidic and, hence, available for EHDL due to the oxygen-induced inhibition of photopolymerization. When

the tribocharged PDMS nanocup array was placed on the pre-textured NOA73 film (Fig. 1d), the troughs of the sinusoidal texture provide periodic recesses in which the NOA73 surface is vertically separated from the tribocharges by a submicron-scale gap. As illustrated in Fig. 1e and Fig. 1f, the crest portion of the sinusoidally textured NOA73 is in direct contact with the tribocharged PDMS nanocup array and, hence, experiences both capillary action and tribocharge's Coulombic attraction. The results are shown in Fig. 2.

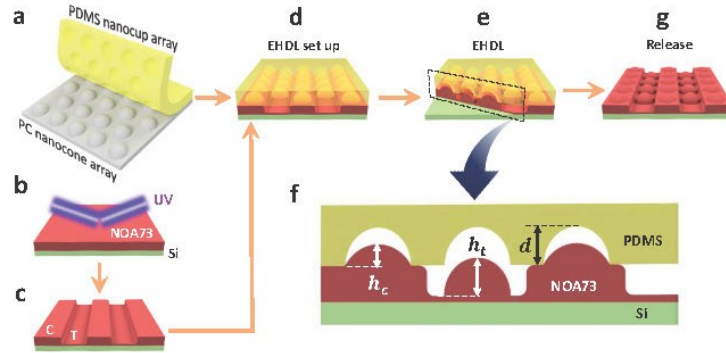


Figure 1 UV-controlled decoration of 2-beam interference pattern through tribocharge-enabled EHDL of photopolymer. (a) Liquid-phase PDMS is poured onto the PC mold textured with a 2D triangular nanocup array. After thermal curing, the PDMS replica, textured with a nanocup array, is peeled off. Its surface becomes selectively tribocharged during the demolding process. (b) A UV-curable photopolymer (NOA73) is spin-coated on a silicon substrate and exposed to a UV two-beam interference pattern. (c) The NOA73 thin film is textured sinusoidally with well-defined crest (C) and trough (T) areas due to local volume shrinkage. (d) The tribocharged PDMS nanocup array is placed on the sinusoidally textured NOA73 film. (e) NOA73 in the trough region is attracted upward by the spatially modulated electric fields originated from the tribocharges and undergoes EHDL. NOA73 on the crest experiences forces from both the capillary action and Coulomb attraction. (f) The cross sectional profile defines the heights of the nanostructures in the crest (h_c) and trough (h_t) areas along with d , the nanocup depth. (g) The final UV-induced solidification of NOA73 and removal of the PDMS nanocup array completes the tribo-EHDL of NOA73.

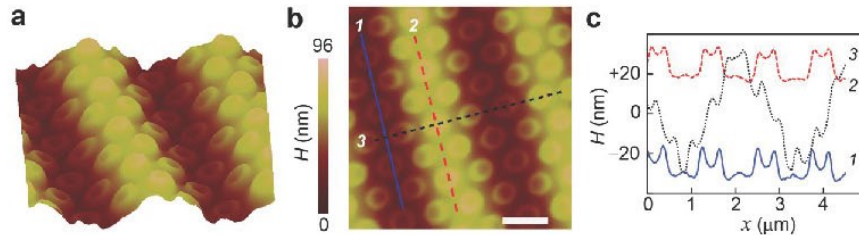


Figure 2 EHDL-generated nanovolcanos forming multiscale metasurface on a 2-beam interference pattern. AFM scans of EHDL results obtained with the UV exposure dose of the two-beam interference lithography set to 3.6 J cm^{-2} . a and b show the final textures in the bird's eye and top views, respectively. c shows their cross-sectional profiles along the lines in b. EHDL resulted in a nanovolcano array (Scale bar: $1 \mu\text{m}$)

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4. References

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