Rapid, Wafer-Scale Laser Nanoprinting of Polymer Surfaces

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ABSTRACT Despite the fact that polymer surfaces are soft, they are notoriously difficult to pattern over large areas on the nanoscale. Two previously described methods, nanoimprint lithography (NIL) and nanosphere lithography (NSL), can be used to nanopattern polymer surfaces, but both of these methods involve many (>6) processing steps. Laser interference patterning (LIP) is a maskless surface nanopatterning technology that has been around for more than 10 years. In this issue of *ACS Nano*, Wang and co-workers demonstrate that LIP can form the basis for a simplified nanopatterning scheme that is general for a wide variety of polymer surfaces. As reported in this issue of *ACS Nano*, laser interference patterning (LIP) has been adapted to the problem of nanopatterning polymer surfaces rapidly and over wafer-scale areas.

Arrays of polymer nanowires can render a surface simultaneously ultrahydrophobic and ultrasticky. Gecko feet, for example, consist of arrays of nanometer-scale protrusions called spatulae that conformally contact rough surfaces promoting adhesion.[1] The surfaces of insect wings and lotus leaves are blanketed by similar protrusions, rendering them ultrahydrophobic and self-cleaning.[2] No array of polymer nanowires imparts these properties, but materials scientists have had considerable success developing surfaces that mimic nature.[3,4] The trouble is that making these surfaces is laborious and requires state-of-the-art nanofabrication technologies such as electron beam lithography. Scaling these nanopatterning processes to wafer-scale areas can be impractical from both cost and process-time perspectives. As they report in this issue of *ACS Nano*, Wang and co-workers[5] have adapted laser interference patterning (LIP) to the problem of nanopatterning polymer surfaces rapidly and over wafer-scale areas. The development of methods to pattern polymer surface on the nanometer-scale has been actively studied for more than 15 years, and I attempt a review of a few prominent methods below, to place Prof. Wang's beautiful results, described later in these pages, in proper perspective.

An elegant approach to the problem of nanopatterning large (cm^2) planar surface areas was advanced by Deckman and Dunsmuir in 1982,[6,7] who showed that contact lithographic masks consisting of close-packed monolayers of spherical polymer beads could be prepared on planar surfaces either by electrostatically driven self-assembly or by spin-coating. Van Duyne and co-workers[8,9] refined this mask formation process and demonstrated in the early 1990s that the evaporation of material onto and through these masks enabled the creation of arrays of nano- and microparticles composed of metals and CaF_2. This approach, called nanosphere lithography (NSL), has been particularly powerful for the fabrication of metal nanoparticle arrays for plasmonic applications.[10] Recently, NSL has been adapted by Kustandi *et al.*[11] to the problem of polymer surface nanopatterning using the following scheme: (1) NSL-patterned chromium particle arrays on silicon are used as etch masks to create arrays of deep ($\approx$1 μm) pits. (2) These pits are backfilled with solution-cast parylene. (3) A second gas-phase etch by XeF_2 selectively removes silicon from the surface, exposing dense arrays of paralene nanofibrils 250 nm in diameter and *ca.* 1 μm in length. Superhydrophobicity is observed for these surfaces. The process flow for this procedure, however, is daunting, comprising seven total steps (see Figure 1a).[11]

Nanoimprint lithography (NIL) encompasses a second family of methods that emerged almost in parallel with NSL in the mid-1990s (see Figure 1b for schematic), but the impact of NIL on polymer surface nanopatterning seems to have been much greater: over 600 publications on this process have appeared to date, many of these involving the nanopatterning of polymer surfaces. Chou, Krauss, and Renstrom are widely regarded as the inventors of this simple but powerful idea.[12,13] In their very first paper describing the process, these practitioners described the preparation of

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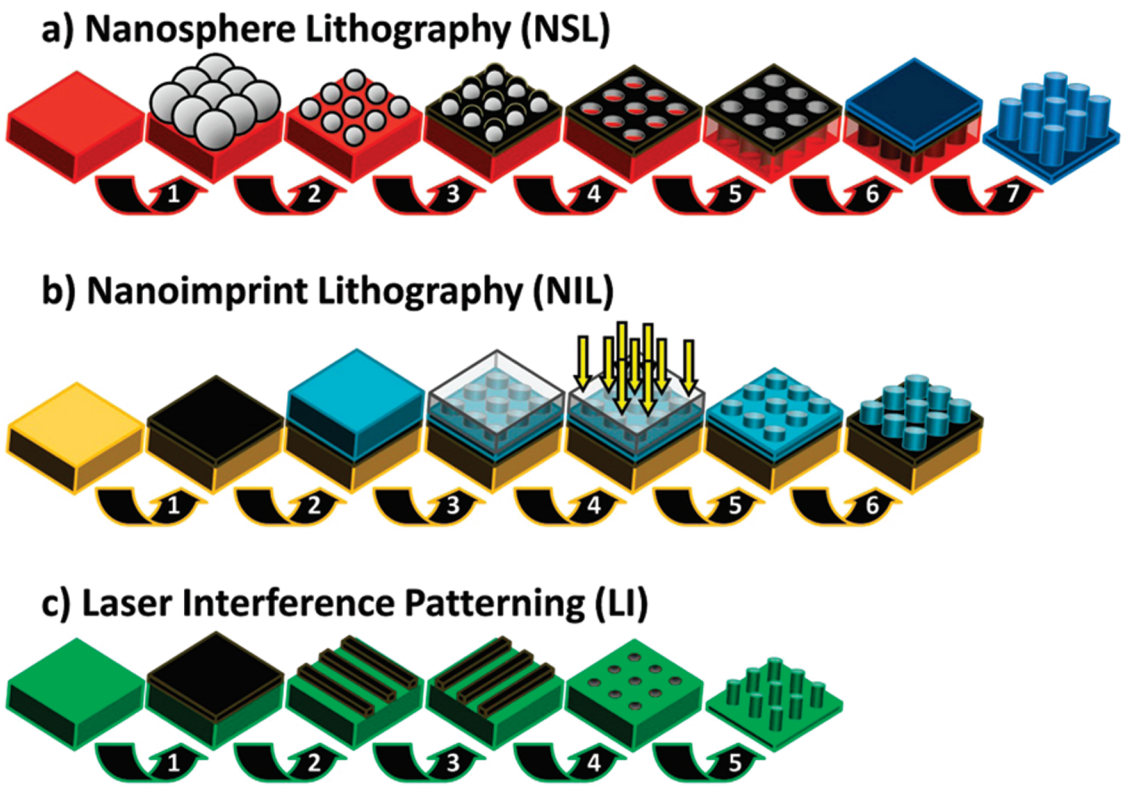

Figure 1. Schematic flow diagrams for (a) nanosphere lithography, (b) nanoimprint lithography, (c) laser interference patterning. (a) Nanosphere lithography (NSL) comprises 7 steps: (1) formation of colloidal monolayers; (2) etching with oxygen plasma; (3) Cr deposition using electron beam evaporation; (4) particle removal by sonication; (5) deep etching; (6) deposition; (7) final etching. (b) Nanoimprint lithography (NIL) comprises 6 steps: (1) mask deposition; (2) coating resist; (3) stamp imprintation; (4) UV exposure; (5) mask removal; (6) residual layer etching. (c) Laser interference patterning (LI) comprises 5 steps: (1) coating deposition; (2) first laser interference patterning; (3) sample rotation; (4) additional laser interference patterning; (5) etching.

25 nm vias and trenches at 60 nm half-pitch in PMMA films,[12] a remarkable accomplishment. In its simplest form, NIP involves just four steps: (1) fabricate a silicon master that has a topography complementary to the desired ultimate pattern; (2) press this master onto a polymer layer that has been heated to a temperature above its glass transition; (3) using reactive ion etching (RIE), remove the polymer from thinned regions; and (4) effect pattern transfer by etching exposed silicon regions. The preparation of the master may involve rather laborious electron beam lithography (EBL) or other similarly intensive methods, but this master can be reused for multiple samples.

Is there a faster and easier way? Wang and co-workers[5] have explored this question by developing a three-step patterning process for preparing arrays of polymer nanofibrils. In the simplest case, their process involves exposing a polymer layer interference lithography (IL). The concept of using the interference pattern from two laser beams to pattern surfaces was first envisioned 15 years ago as a means for patterning ferromagnetic materials for fundamental investigations of perpendicular magnetic storage at the nanoscale. The IL process exploits the interference of two laser beams with wavelength, λ, intersecting at an angle, θ, on a photoresist-coated substrate. Interference between these two beams produces a standing wave pattern consisting of a linear array of intensity maxima and minima having a period $\lambda/(2 \sin \theta)$.[14] A single exposure produces an array of lines at the standing wave period, but by rotating the sample by 90° and exposing a second time, an array of holes is produced in the resist. The two-dimensional ordering of the nanoparticles, nanoposts, or nanowire arrays produced by IL is limited to square, hexagonal, or oblique patterns, but the advantages of IL are that it is a maskless, parallel process that can efficiently pattern areas of over 10 cm^2.[14] These advantages were apparent from the earliest papers on IL, in the late 1990s; initial demonstrations of nanostructure formation using IL involved the fabrication by Smith, Savas, and co-workers[15,16] of large area (10 cm^2) arrays of dimensionally uniform gold posts with diameters of 35 nm and lengths of 100−200 nm. These post arrays were obtained by operating on PMMA resists with 193 nm laser illumination, effecting pattern transfer to the underlying SiO_2 by etching, and finally electroplating gold into the resulting voids from an electroless seed layer. Working with Savas at MIT, Ross and co-workers[14,17] adapted this

method to the formation of arrays of ferromagnetic Co, Ni, and CoNi alloy posts with diameters of 180 nm and lengths of 200−300 nm.

Two variants of IL for nanopatterning polymer surfaces have been devised by Wang and co-workers:[5] In the simplest version, a layer of UV-absorbent polymer (*e.g.*, polyethylene terephthalate) is directly patterned twice to produce a latent image of a nanowire array within the film (see Figure 1c). Then, RIE is carried out to remove the unexposed polymer from the pattern, exposing polymer nanowires. Arrays of 300−500 nm diameter Dura film wires were obtained at 500 nm pitch using this approach. A second variant of the process can be used to pattern polymers that are not UV-sensitive (*e.g.*, poly(dimethylsiloxane) or PDMS). In this case, a photoresist (PR) layer is overlaid on top of the polymer layer; it is patterned twice and developed to produce an array of PR nanodots, and these PR dots are used as an etch resist to preserve the underlying polymer while RIE is used to remove the unprotected polymer, again resulting in the formation of a nanowire array. Nanowire diameters of *ca.* 1.0 at 1.0 μm pitch are demonstrated for this more complex process, in the case of PDMS. Especially in view of the spectacular results achieved using IL for metals (see above) and NIL for a variety of materials, an important question is which of the two process steps—writing or developing—limits the resolution seen in polymer surface patterning by IL? When this critical issue is resolved, it is likely that even higher resolution will be recoverable for the nanopatterning of polymer surfaces using IL.

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