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Replication of Vertical Features Smaller than 2 nm by Soft Lithography

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This communication describes the use of soft lithography to replicate features with vertical dimensions <2 nm. This demonstration is particularly interesting because these dimensions are those of large molecules. The sizes of the features that can be replicated by replica molding are thus beginning to overlap the sizes of molecules that can be generated by organic synthesis. This overlap represents a step in fusing "top-down" and "bottom-up" approaches to nanofabrication.

Soft lithography has been demonstrated previously for the replication of ~10-nm horizontal features.[1] We wished to measure the ability to replicate smaller features using a poly(dimethylsiloxane) (PDMS) stamp. To carry out this measurement, we needed both an appropriate test structure and a corresponding measurement technique. We chose atomic force microscopy (AFM) for the measurements because this technique can measure vertical displacements with <1 Å resolution. A characteristic of scanning probe microscopy is that the results are difficult to interpret when the features being measured have shapes that cannot be accessed by the tips; in these instances, in effect, the feature measures the shape of the tip, rather than *vice versa*.[2] The smallest probe tips are carbon nanotubes, but even they have a radius of curvature of at least 2 nm, and therefore yield ambiguous results in measuring recessed features with comparable dimensions.[3] We required a sample whose topography had two characteristics: (i) features with a low aspect ratio (that is, features that were broad relative to their height) so that there would be no issues in deconvolving the shape of the features from that of the probe tip, and (ii) a periodic structure to increase the signal-to-noise ratio (S/N). We have used features written in poly(methyl methacrylate) (PMMA) using an electron beam *without development following exposure*.[4] This type of writing generates small (1 to 10-nm vertical displacements), broad (~100-nm half-width) grooves in 200-nm thick films of PMMA.[5]

We wrote a series of parallel lines with a 250-nm pitch. Figure 1A shows a tapping mode AFM image of a sample and a corresponding cross-sectional scan of the pattern. The lines increase in depth from left to right as the electron dose increased from ~10 to ~550 electrons/nm^2 in steps of 27 electrons/nm^2. Overlap of neighboring lines decreases the height of the ridge between the grooves and generates a sloped baseline (Figure 1A). The line with the highest electron dose is ~6 nm deep, but is actually ~12 nm below the original surface of the thin film. Primary electrons have the highest flux in the center of the intended write region, but secondary electrons (backscattered) and irregularities in the electron beam probably broaden the exposed region of PMMA resist.[6]

A minimum feature depth of ~0.5 nm (left-most line) is visible from the AFM image, but is not easily discernible from the cross section. A depth less than 1 nm is close to the surface roughness of the PMMA (±0.45 nm);[7] the regular, periodic structure of the lines makes features of this size easy to recognize.

We fabricated composite elastomeric molds with a "hard" poly(dimethylsiloxane) (*h*-PDMS) layer in contact with the PMMA surface.[8,9] The surface tension of an elastomeric stamp can cause rounding of sharp edges, but a composite stamp with a *h*-PDMS surface seems to replicate these features well.[9] We spin-coated *h*-PDMS onto the patterned PMMA surface and partially cross-linked the elastomer before adding a soft PDMS backing.[10] After curing the composite elastomer, we gently released the mold from the PMMA surface while holding the PDMS with a pair of tweezers. This PDMS mold was directly imaged by AFM (Figure 1B). The surface roughness of the PDMS (±0.49 nm) was similar to that observed for the original PMMA film.

We transferred these test structures into polyurethane (PU) by replica molding the PDMS stamp. The composite stamp separated

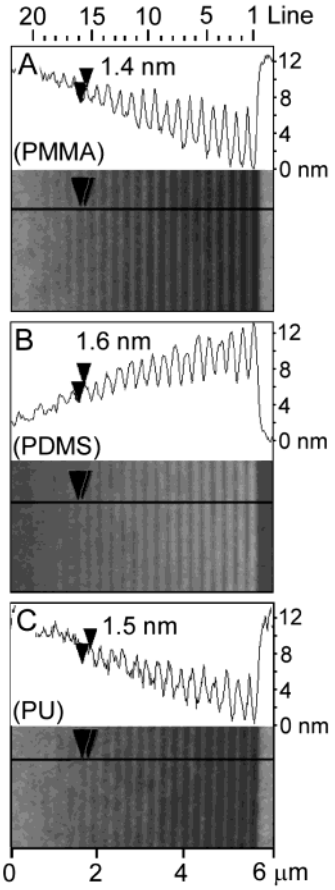

Figure 1. Tapping mode AFM images of parallel lines spaced by 250 nm with a varying vertical displacement from ~0.5 to ~5 nm deep in (A) a 200-nm thick PMMA film, (B) *h*-PDMS, and (C) UV-cured polyurethane. We fabricated the original test structure by direct exposure to a focused electron beam at 30 kV (30 μm aperture, 160 pA beam current, ~20-nm beam spot size) with a gradually increasing dose of electrons (left to right) of ~10 to 550 electrons/nm^2. The vertical displacement of the fifth line from the left, as indicated in each image, is replicated with high fidelity using soft lithography.

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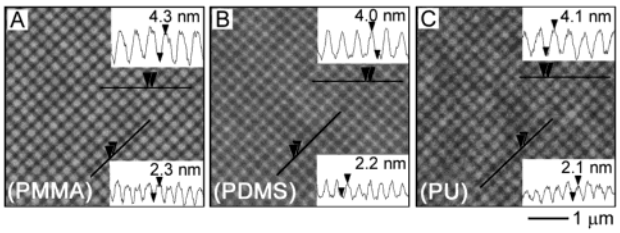

Figure 2. AFM images of (A) PMMA test structures generated by writing a grid of crossed lines with an electron beam (~200 electrons/nm^2, 30 kV), (B) the corresponding mold in *h*-PDMS, and (C) a PU replica. The parallel lines, spaced by 250 nm, are ~2 nm deep except where the lines intersect with a depth of ~4 nm.

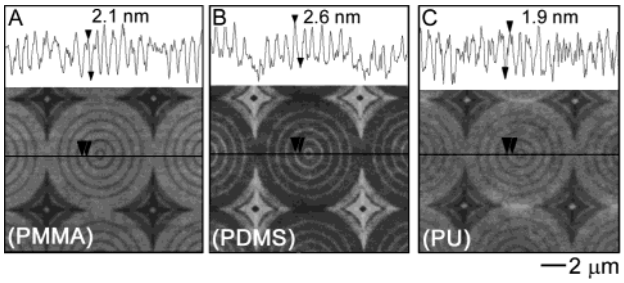

Figure 3. A series of concentric circles and pyramids, as imaged by tapping mode AFM, in (A) a 200-nm thick PMMA film, (B) *h*-PDMS, and (C) UV-cured polyurethane. We fabricated the original test structure by directly patterning the PMMA with a focused electron beam (~200 electrons/nm^2, 30 kV). Cross sections for the circular patterns are shown for each substrate. The circles have a vertical displacement of ~2 nm; the pyramids are composed of displacements from ~2 nm at the periphery to ~9 nm toward the center. The line spacing decreases toward the center of the pyramidal shapes, creating a sloped wall from the overlapping electron beam exposure. At the center of the pyramid is a post (or hole in B) where the PMMA was not exposed to the electron beam. (Further perspectives and line scans of these substrates are provided in the Supporting Information.)

easily from the polyurethane replica. This polymeric replica exhibited a surface roughness of ±0.70 nm, however, a roughness ~1.5 times that of either the PMMA master or the *h*-PDMS replica. We attribute this roughness of the polyurethane to its inelastic deformation upon separation due to surface interactions between the master and replica. Separating the polyurethane replica from the PDMS stamp while the two were immersed in methanol decreased the surface roughness of the replica to ±0.52 nm,[11] a value indistinguishable from that of the PMMA or *h*-PDMS structures. The AFM image of the polyurethane replica (Figure 1C) showed a uniform template-mold interface, with no trapping of air bubbles during the replication process. The test structure of the replica also matched the original template. For example, the fifth line from the left in Figure 1C was similar in depth (1.5 nm) to that in the original PMMA structure (1.4 nm, Figure 1A).

Structures with other shapes and topographies could also be directly written into a PMMA film and replicated using the procedures described in this paper. The dependence of feature depth on the electron dose was apparent at the intersection of two intersecting lines. Crossed lines in PMMA each with a ~2 nm vertical displacement, written with a continuous dose of ~200 electrons/nm^2, had an ~4-nm displacement at their intersection (insets, Figure 2A). The *h*-PDMS mold of this template (Figure 2B) showed an array of ~4 nm "spikes" of *h*-PDMS on an array of ~2 nm lines. The PU replica (Figure 2C) closely resembled the initial PMMA template. The replication of nanoscale features by soft lithography also extends to more complex structures. Figure 3 shows a series of pyramids arranged in a square lattice around a group of concentric circles. The structures in Figures 2 and 3 demonstrate the replication of regular patterns of features with well-defined heights and lateral positions.

This work indicates that soft lithography using *h*-PDMS will reproduce low-aspect ratio structures with vertical topography having features ≥1 nm. It is thus possible to replicate and image structures with vertical dimensions on the molecular scale; whether it is possible to replicate molecules themselves remains to be established experimentally. With present methods, noise in the system (surface roughness of the polymers, perhaps due to inelastic deformation on separating the mold and replica and atomic-level granularity in the materials) makes it impossible to see features smaller than 1 nm; we will, however, continue to develop the methods, and we believe that smaller features will be accessible using materials different than those we have used, since, in principle, the resolution is limited by the smallest distance between molecules of the template and mold. This limit is 0.165 nm or less as determined by van der Waals forces for two surfaces in contact.[12]

The manufacture of nanostructures moves closer to reality with the development of tools that can replicate patterns extending over large areas rapidly and at low cost. This work establishes the replication of vertical dimensions down to ~2 nm by soft lithography. The use of electron beam writing in PMMA without subsequent development provides a useful new method to fabricate samples for this type of metrology. The limit to the replication of lateral dimensions remains to be established, and requires a more elaborate method of measurement than AFM to avoid artifacts due to interactions between tip and sample.

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Supporting Information Available: AFM images complementary to Figures 1 and 3, and experimental protocols for the fabrication of the polymer test structures and the replication process (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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