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Chemically Nanopatterned Surfaces Using Polyelectrolytes and Ultraviolet-Cured Hard Molds

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ABSTRACT

Polymer transfer printing of poly(acrylic acid) onto a polyelectrolyte multilayer platform resulted in chemically nanopatterned surfaces with well-defined structures and both positive and negative surface functionalities. A commercially available urethane-related photopolymer cured by ultraviolet light was used to make stamps for contact printing with a range of submicrometer down to 80 nm features because of its outstanding mechanical stability and inherent softening transition above 48 °C.

Micro- and nanometer-scale chemical patterns are indispensable and ubiquitous in a range of applications such as electronic devices,[1,2] electrooptical devices,[3] (bio)chemical sensors,[4] and proteomic or genomic arrays.[5] Our laboratory developed polymer-based printing methods such as polymer-on-polymer stamping,[6] multilayer transfer printing,[7] and polymer spin transfer printing[8] to introduce patterned chemical functionalities with micro- to nanoscale features onto an extended range of surfaces including nonplanar, polymeric, and biosurfaces. On the basis of the contact-printing concept of transferring inks from stamps to substrates but surpassing the limitations of conventional microcontact printing in applicable surfaces, our polymer transfer printing techniques have provided a unique way to incorporate chemical patterns into devices utilizing polymeric inks and polyelectrolyte multilayer substrates.

The ability to pattern polymeric inks down to below 100 nm has been a persistent challenge because of the size and multivalent nature of the macromolecules and the need to control their interactions with the substrates and stamps. In this letter, we introduce a convenient means for chemical nanopatterning in a size range of submicrometer to below

100 nm using a hard stamp prepared from an ultraviolet-(UV)-curable polymer, a polyelectrolyte ink, and a polyelectrolyte multilayer platform. In the process schematically illustrated in Figure 1, a polyanion, poly(acrylic acid)(PAA), was first spin-coated onto the stamp, and then the stamp was brought into contact with the oppositely charged surface of a [poly(allylamine hydrochloride)(PAH)/PAA]$_n$ multilayer built onto substrates. Spin-coating ensures the uniform distribution of the polymer ink onto the stamp surface, and the hard stamp maintains the nanosized features without collapse during contact printing. The process results in finely nanopatterned surfaces with both cationic and anionic functionalities. Importantly, our polymer transfer printing processes can be applied to virtually any substrate on which polyelectrolyte multilayers can be formed or surface charges preexist.

Nanometer-scale printing processes rely significantly on stamp molding technologies. Poly(dimethylsiloxane) (PDMS), the conventionally used stamp material in soft lithography,[9,10] has shown great performance in micrometer-scale processes. However, limited aspect ratios, due to sagging and pairing, and poorly replicated nanofeatures, due to the inherent softness and mechanical failure above its glass-transition temperature, remain substantial drawbacks in using PDMS for submicrometer features.[11,12] To solve these problems, many approaches have been developed for a mold material harder than soft PDMS using composites[13−16] or newly highlighted UV-curable photopolymers.[17−21]
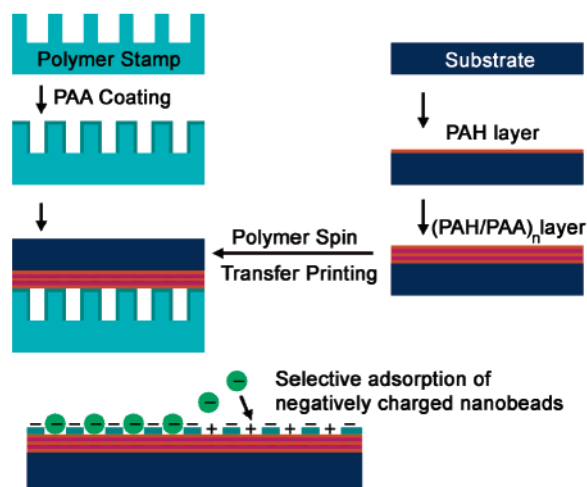
A commercial UV-curable polymer (Norland Optical Adhesive (NOA) 63, Norland Products Inc.) is suitable for

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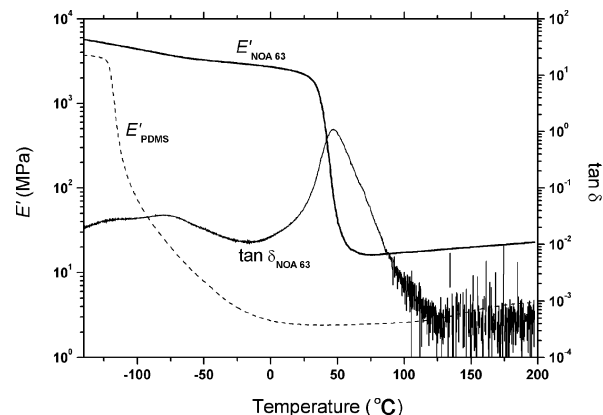
Figure 1. Polymer spin transfer printing process.

Figure 2. Temperature dependence of tensile storage moduli (E') for NOA63 (—) and PDMS (- - -) and the loss tangent for NOA63 (—).

nanometer-scale contact printing and imprint lithography. NOA 63, originally developed as an optical adhesive, has excellent optical properties over a wide spectral range (refractive index 1.56 and transmission above 98% in a wavelength range from 360 to 1260 nm) and strong mechanical properties. It loses its adhesive bonding property above 60 °C when used as an adhesive for glass, which is important to consider for replica molding. Thus, it can be cured on an etched silicon master containing nanopatterns and peeled off at higher temperatures, producing molds with replicated patterns. The most significant advantage of NOA 63 for nanometer-scale contact printing is that it is a urethane-related polymer cured by mercapto-related cross-linking reagents and UV light. The urethane-related stamp becomes soft enough to make conformal contact between the stamp and substrate upon reaching a glass-transition temperature around 50 °C while still maintaining mechanical properties sufficient to withstand deformation during the process. These phenomena originate from the dissociation of physical cross links in polyurethane chains and the retention of covalent cross links at high temperatures, resulting in elastomeric properties.

Figure 2 shows the thermal transition of the tensile storage modulus and the loss tangent for NOA63 in the temperature range of −140 to 200 °C measured by dynamic mechanical analysis (ramping rate ~3 °C/min, amplitude ~15 μm, frequency ~1 Hz, DMA model Q800, TA Instruments). In the plot of the loss tangent, NOA63 exhibits α and β relaxations at 48 and −75 °C, which correspond to hard and soft segment relaxations in the polyurethane, respectively. Above the α relaxation, the tensile storage modulus of NOA63 increases linearly, indicating a chemically cross-linked elastomeric structure. Remarkably, the storage modulus values (16.2−22.9 MPa) of NOA63 in the temperature range where it shows elastomeric properties are 5−7 times larger than that of PDMS (2.4−4.5 MPa, Sylgard184, Dow Chemical, 10:1 prepolymer/curing agent, cured at 60 °C for 12 h).

Polymer stamps used in this study were prepared by casting NOA 63 onto etched silicon masters with various topographical features, followed by curing with UV light

(wavelength ~365 nm) for 3 h. The stamps that were cured and peeled off of the masters showed good replication of the original masters with high aspect ratios. Figure 3A shows scanning electron microscopy (SEM, JEOL 5910) images of a stamp that has a high aspect ratio of 2.8 up to 6.7. The images confirm an excellent replication of the original nanopatterns, although the SEM measurement of the sectional area of the polymer stamps in the images is slightly deformed because of the exposure to the high energy of the electron beam. This replication could be carried out for very dense 70 nm line/space patterns with an aspect ratio of 1, as shown in Figure 3B and C, demonstrating that sub-100-nm molding was also successful by using NOA63.

Before the spin-coating process, the surface tension of stamps was further decreased by surface modification, and multilayer platforms were formed on silicon substrates. Chemically active functionalities on the stamp surfaces (mainly secondary amines in the urethane units) were passivated by reacting them with (tridecafluoro-1,1,2,2,-tetrahydrooctyl)-1-trichloro silane vapor (United Chemical Technologies Inc.). As a result, the stamps had defined surface properties (surface energy decreases from 53.1 to 43.2 mN/m) and reduced adhesion to the spin-coated polyelectrolyte ink. To prepare the chemically functional multilayer platform, a silicon substrate cleaned under oxygen plasma (100 W, 0.3 Torr, 5−10 min, Harrick Scientific Co. model PDC-32G) was alternatively submerged into aqueous solutions of a polycation/polyanion pair, PAH (10 mM based on its repeat unit, M_w = 70k, Aldrich Chemical Co.)/PAA (10 mM, M_w = 90k, Polysciences Inc.), starting with the PAH solution. The final platform after a 2.5 bilayer assembly process results in a PAH top surface that provides a cationic surface that is able to react with the anionic polymer ink of PAA. The creation of chemically modified surfaces using the multilayer assembly process can be applied to any kind of substrate after plasma treatment if necessary, which makes our polymer transfer printing processes widely applicable.

The dimensional stability of NOA stamps was evaluated using an equation developed by Hui et. al.,[12] which shows how prepared stamps were stable during a contact printing process without serious deformation. For a defined nanofea-
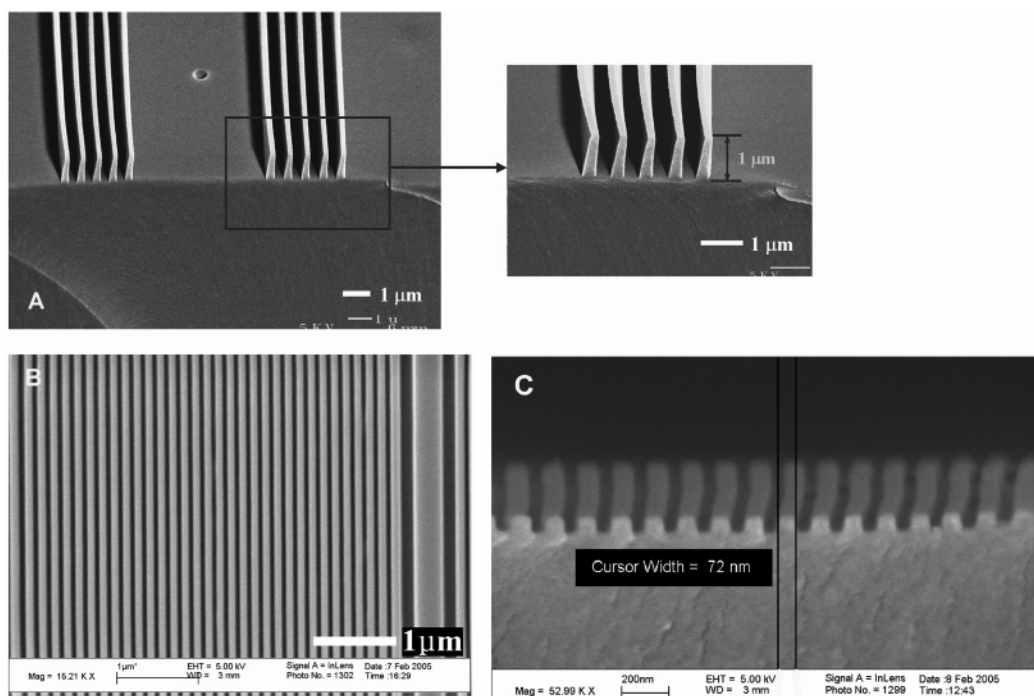
Figure 3. SEM images of the UV-cured polymer stamp including nanostructures (A) with a high aspect ratio of 2.8 to 6.7, line/space sizes from 350/350 to 150/150 nm, and 1 cm length. Enlarged images show that the height of the structures is around 1 micrometer. (B, C) 70 nm line/space patterns.

ture with width $2a$, spacing $2w$, and height h, the stability for lateral collapse increases with elastic modulus E (obtained from E' and tangent loss data) and decreases with increasing surface tension γ. Thus, by determining appropriate patterned structures, varying E with the processing temperature, and modifying the stamp surface chemistry to change γ, we could control the dimensionless stability parameter calculated by the below equation to be less than 1, which indicates good dimensional stability. As an example, the parameter value was 0.82 when we used stamps containing nanofeatures with a width of 150 nm, spacing of 150 nm, height of 400 nm, elastic modulus of 32.3 MPa at 55 °C, and surface tension of 43.2 mN/m.

$$\frac{h}{\sqrt{4wa}}\left(\frac{\gamma}{2Ea}\right)^{1/4} < 1$$

PAA (50 mM, pH 3.4) was spin-coated on the prepared stamps at 3000 rpm for 30 s and used for contact printing. The transfer printing process was carried out on a hot plate where the temperature was controlled at 55 °C. First, both the substrate coated with a multilayer and the polymer stamp with spin-coated polymer ink were placed on the hot plate for 1−2 min to soften the stamp. Then the stamp was put onto the substrate for 1−2 min with slight pressure and peeled off while hot. With this process, only the parts of the stamp that made conformal contact with the substrate surface were transferred to the substrate. An example of the resulting nanopatterned surfaces, investigated by using atomic force microscopy (Veeco Instruments, Dimension 3000), is shown in Figure 4A. Polymer ink that was uniformly applied to a stamp with positive features of various line/space sizes (350/
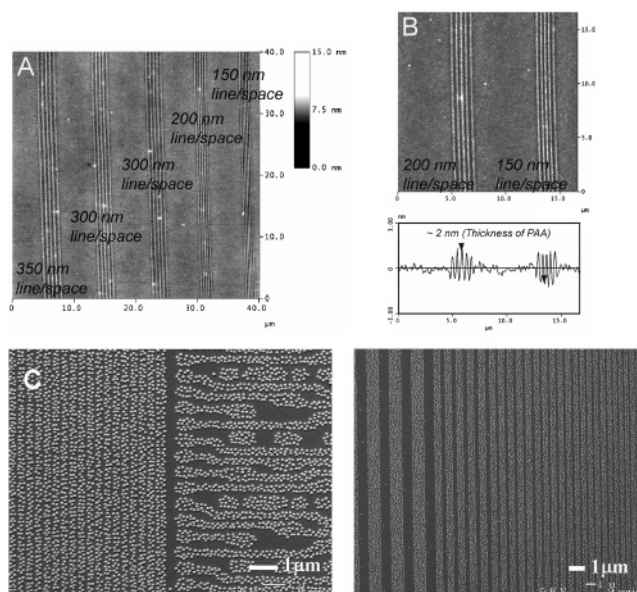
Figure 4. Atomic force microscopy images of poly(acrylic acid) (PAA) nanopatterns on the poly(allylamine hydrochloride) (PAH) top surface of a $(PAH/PAA)_{2.5}$ multilayer. (A) Line/space of PAA patterns. (B) Enlarged images of 200/200 and 150/150 nm line/space patterns with a transferred pattern thickness of around 2 nm. (C) SEM images of polystyrene nanobeads (∼96 nm) deposited on complex micro- and nanoscale chemical patterns containing grating width and space.

350, 300/300, 300/300, 200/200, and 150/150 nm) was successfully transferred onto the substrate surface via this simple printing process. The length of these line patterns was 1 cm, suggesting larger area applications. As shown in the enlarged and sectional images (Figure 4B), the pattern edges were well defined, and the thickness of the transferred

patterns was around 2 nm. It should be noted that the UV-cured polymer stamp with precise nanometer-scale features was mechanically stable over the entire process.

Active functionalities of both positive and negative charges were verified by studying the selective adsorption of negatively charged polystyrene beads (∼96 nm, sulfonated groups on the surface, Interfacial Dynamics Co.) onto the polycation (PAH) surface that did not contact the stamp during the printing process. The negatively charged beads were not adsorbed onto the transfer-patterned area because of electrostatic repulsion. SEM images in Figure 4C demonstrate various patterns of adsorbed beads. Particles were associated on mixed patterns of lines and complex shapes and on the lines with grating widths in Figure 4C. In all of the images, we could see that the sizes of patterns on which particles were not adsorbed approached 80 nm, thus confirming the successful chemical patterning of PAA in the range below 100 nm.

In summary, we introduced the use of a commercial UV-curable material as a mold in contact printing processes and imprint lithography and applied it to our polymer transfer printing process to achieve chemically nanopatterned monolayers in the submicrometer range down to 80 nm. Thus far, we do not believe that we have reached the physical limit for the patterning of polymer; the dimension of 80 nm was that available for these investigations and smaller dimensions will be tested in future work. Because the UV-cured polymer has outstanding optical and mechanical properties as well as a softening transition at mild temperatures, it is highly likely that in addition to contact printing processes the polymer can be applied to various other applications in nanometer-scale soft lithography. Our polymer transfer printing technique using a polyelectrolyte ink suggests a number of possible applications, including the patterning of (bio)functionalized copolymers with polyelectrolyte blocks that are reactive with polyelectrolyte multilayer surfaces or the surface-directed assembly of nanoparticles with magnetic, optoelectronic, and biorelated functionalities onto chemically nanopatterned surfaces without limitation for applicable surfaces.

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