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High density nanostructure transfer in soft molding using polyurethane acrylate molds and polyelectrolyte multilayers

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Abstract
Here we present an alternative, new, unconventional lithographic technique developed to create dense and multilevel nanostructure pattern transfer using a highly accurate polyurethane acrylate (PU, MINS101m, Minuta Tech.) mold and a polyelectrolyte multilayer as the adhesion promotion layer. Specifically, we demonstrate the pattern transfer of periodic 80 nm lines with 400 nm height and complex and multilevel nanostructures to a polymer layer on various substrates, such as Si or SiO_2 wafers, glass and flexible polymer films. This new, unconventional lithographic technique presented here would open the door to a variety of applications in the fields of electronic, optical and biological devices.

The fabrication of electronic, optical and biological devices requires the patterning of surfaces on micro- and nanometre scales. Currently the dominant technology for micro- and nanostructure fabrication is photolithography. However, the cost of short-wavelength light sources and photosensitive polymer (photoresist) increases rapidly with diminishing resolution limit. As the required feature size is reduced further, photolithography will eventually reach its limits. Unconventional lithographic techniques such as soft lithography [1] and imprint lithography [2] have been developed as alternatives for photolithography and utilized successfully in a number of applications in materials science [3, 4], including flexible displays [5].

Over the past decade extensive efforts have been made to replace photolithography with unconventional patterning techniques. A number of promising low-cost techniques that have been developed recently involve a form of soft lithography [1]; such methods involve the use of an elastomeric master that is used to transfer a pattern, including micro-contact printing, replica molding, micro-transfer molding, and micro-molding in capillaries. Recent additions to these nonlithographic approaches include 'dip-pen' nanolithography [6], soft molding [7, 8], capillary force lithography [9], polymer-on-polymer stamping [10] and patterning techniques using de-wetting of a thin polymer layer [11].

The majority of these soft lithography techniques utilize a polydimethylsiloxane (PDMS) mold, which presents some advantages. In particular, PDMS reproduces nanoscale structures with great fidelity. Also, there is generally poor adhesion between the PDMS mold surface and the polymer to be molded [1], allowing complete release from the mold. However, with regard to nanostructure fabrication, the use of a PDMS mold has some disadvantages. Although soft-lithography methods such as replica molding, micro-molding in capillaries and others can make isolated line and ring structures at the nanometre scale, it is generally difficult to produce a densely arrayed nanopattern (e.g. alternating 100 nm line/space) because the PDMS mold collapses laterally [1]. Recently, researchers in the Whitesides group improved the pattern fidelity using a hard PDMS mixture; the process involves the construction of a two-component stamp consisting of a soft, thin PDMS layer and a thicker, harder, more highly cross-linked polysiloxane as a support [12]. This approach alleviates a number of the issues of collapse, but requires the construction of a more complex elastomeric mold.

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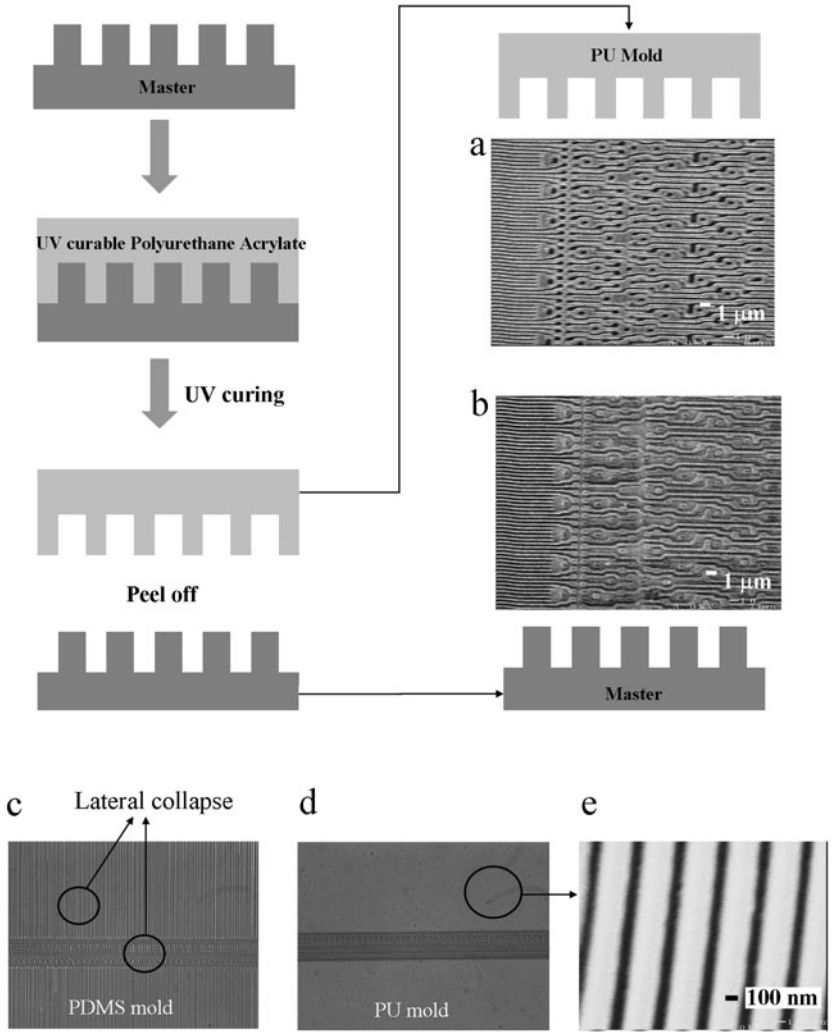

Figure 1. An illustration of the procedure for fabricating a PU mold from the master. SEM images of (a) a replicated PU mold and (b) a master. Optical microscopy images (500×) show the good fidelity of the PU mold in nanostructure replication: (c) is the laterally collapsed PDMS mold; (d) is the PU mold in replication of the same master; (e) shows periodic 80 nm lines in the PU mold.

The use of a completely hard mold has been demonstrated with imprint lithography, which has the unique feature that it can be used to create especially dense nanostructures [2]. Although imprint lithography is a promising technique for nanostructure fabrication, some challenges to overcome include problems in release due to strong adhesion between the hard mold and the polymer layer on the substrate [13], variations due to changes in the pattern density [13, 14], and limited material transport [15]. Imprint lithography with a high-aspect-ratio mold can induce deformation of the polymer layer on the substrate by adhering to the stamp [14] and uneven substrates can be broken by the high pressure required for the technique.

In this report, we present a simple method for multi-step nanopattern fabrication with a high feature density. This method overcomes the difficulties and shortcomings of PDMS-based soft lithography and hard-mold-based imprint lithography. We use a combination of a UV-curable polyurethane acrylate mold, the soft-molding process utilizing water soluble sulfonated polystyrene (SPS), and multilayer deposition [16] for the creation of an adhesion promotion layer between the polymer layer and the substrate.

The first step is to fabricate a highly accurate elastomer mold using UV-curable polyurethane acrylate (MINS101m, Minuta Tech.). Figure 1 illustrates schematically the process of forming the polyurethane acrylate (PU) mold, and a comparison between PU- and PDMS-molded stamps. The PU mold is harder than the general PDMS mold (the Young's modulus of the PU mold is $\sim 1.7 \times 10^9$ N m^{-2} at 15 °C). However, the PU mold softens dramatically upon reaching a temperature of 50 °C. At this softening temperature, the mold becomes conformal with the underlying polymer film that is to be molded. A comparison of the master (figure 1(a)) with the PU mold (figure 1(b)) reveals that the original master is replicated with high fidelity. The PU mold has two distinct differences from the PDMS molds typically used in soft lithography. First, in the PU mold it is possible to make a highly accurate mold with a defect-free, dense nanopattern. Figures 1(c)–(e) show the effectiveness of the PU mold with dense nanostructures. The nanostructures in a PDMS mold

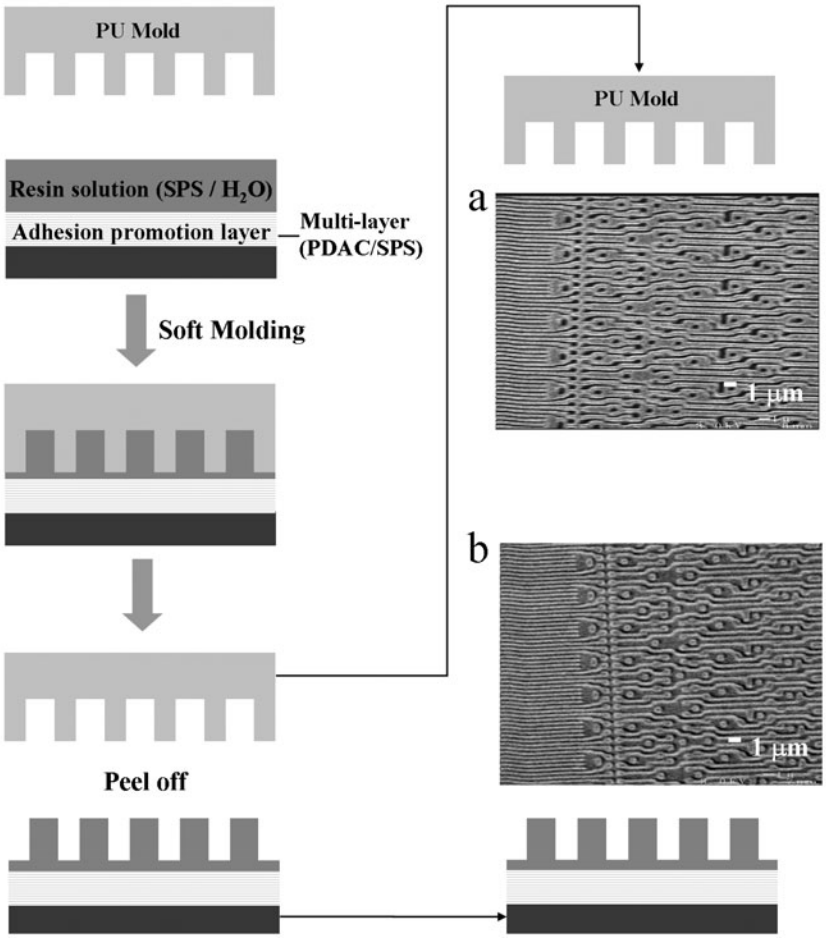

Figure 2. An illustration of the procedure for fabricating a replica on a substrate from a PU mold: SEM images (a) PU mold, and (b) a replicated polymer nanopattern on silicon substrate.

made from the same master collapse laterally (figure 1(c)). However, the PU mold shows good fidelity of the master replication (figure 1(d)). Figure 1(e) shows periodic 80 nm line patterns of the PU mold at higher magnification.

The second step is the transfer of the pattern from the PU mold to a polymer resin. To transfer the nanopattern of the PU mold to a polymer layer on a substrate, the soft-molding technique reported previously has been used [7]. This technique utilizes the absorption of solvent during the molding process of a spin-cast polymer film containing residual solvent. In this case, a 20 wt% aqueous solution of SPS was used as the resin solution. This selection was advantageous for the use of the PU mold because the polyurethane acrylate is permeable to water vapour, providing for absorption and evaporation of the residual solvent under the molding conditions.

We used a polyelectrolyte multilayer (polydiallydimethyl ammonium chloride (PDAC)/(SPS) layer) as an adhesion promotion layer. Using this polyelectrolyte multilayer as an adhesion promotion layer, it is possible to transfer nanopatterns in a polymer layer onto essentially any substrate, such as Si or SiO_2 wafers, glass and flexible polymer films, without defects. The multilayer is prepared via an alternating adsorption process [16]. In this case, the substrate is briefly exposed to an O_2 plasma and then dipped into a solution of polycation (20 mM (PDAC)) for 20 min. The samples are then rinsed with deionized (DI) water and then submerged in a polyanionic dipping solution (10 mM SPS and 0.1 M NaCl) for 20 min. The samples are then rinsed again with DI water. A single bilayer can effectively be used to obtain adhesion to the desired surface. As PDAC and SPS are strong polyelectrolytes [17], they serve as an adhesion promotion layer for the upper SPS layer during the soft-molding process; the SPS at high concentrations is found to adhere well to the SPS of the polyelectrolyte bilayer, whereas the PDAC forms a highly effective adhesive connection between the negatively charged plasma-treated substrate and the top SPS layer. The multilayer is equally effective as higher numbers of bilayers, and adhesion promotion takes place regardless of whether PDAC or SPS is the top layer. However, at least two layers are required to achieve adhesion.

Figure 2 illustrates the transfer process. The warm PU mold at 50–60 °C is placed onto an SPS film immediately after the film is spin-coated (500–1000 rpm, 10 s) onto a substrate from a 20 wt% SPS aqueous solution. At this point the spin-coated film is still wet with residual water (25–35 wt% SPS wet films). The PU mold is then pressed lightly onto the surface of the SPS film, and the PU mold and substrate are allowed to remain in contact undisturbed for a period of time (∼20 min)

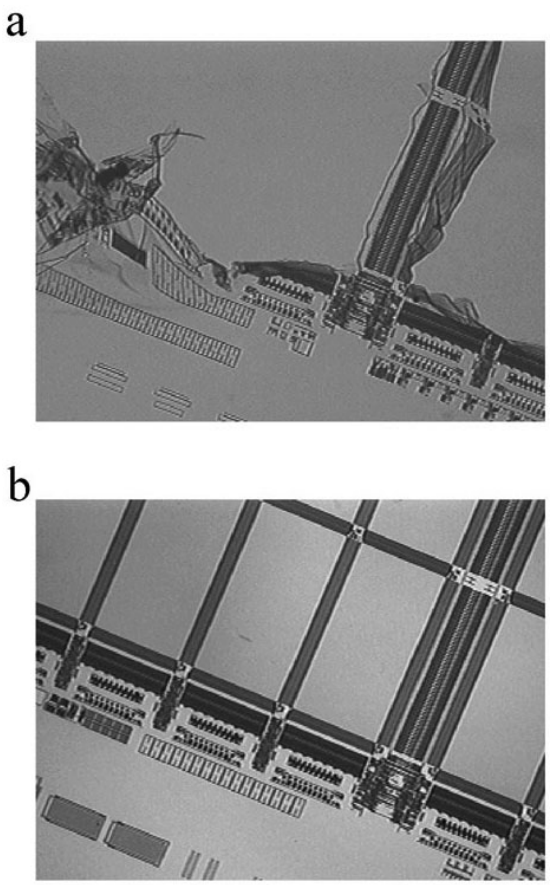

Figure 3. Optical microscopy images (×200) of a polystyrene pattern on bare glass substrate (a), and an SPS pattern on glass substrate treated by a polyelectrolyte multilayer as an adhesion promotion layer (b).

on a hot plate at 50–60 °C. The PU mold is then peeled off the substrate while hot. In this soft-molding process, the solvent absorption of the PU mold is an important factor. According to our experiments, the PU mold can absorb 1% of its weight in water at 50 °C. About 90 wt% of the absorbed water diffuses out into air in 30 min at 50 °C. The PU mold was used more than 10 times without any treatment. A comparison of the PU mold (figure 2(a)) with the transferred nanopattern (figure 2(b)) reveals that the pattern of the PU mold is well replicated in the SPS layer that is transferred to the substrate.

As soft molding takes advantage of the absorption and then evaporation of solvent in the PU mold during the molding step, we can transfer the pattern to a polymer layer with excellent fidelity. In imprint lithography, to get a dense nanopattern with a high aspect ratio is difficult because of the strong adhesion between the polymer layer and the hard mold [13], and the process is often influenced by pattern density [14], limited material transport [15] and high pressure. However, our reported technique overcomes these shortcomings of imprint lithography because the PU mold has stable surface properties, low adhesion with the polymer layer to be molded, and because soft molding promises a high-fidelity pattern transfer [7]. Also, we can easily, cheaply and repeatedly fabricate the PU mold from the original master. The use of the polyelectrolyte multilayer as an adhesion promotion layer makes it possible to fabricate nanopatterns on various substrates such as Si or SiO_2 wafers, glass and flexible polymer films. In figure 3 we show the importance of the polyelectrolyte multilayer as an adhesion promotion layer. Although the PU mold has stable surface properties, the dense nanostructures formed from the PU mold detach when transferred directly to glass (figure 3(a)). Figure 3(b) illustrates the complete transfer and stability of the pattern when transferred onto the multilayer. We can tune and tailor the surface properties of the top layer in multilayer deposition to optimize the adhesion of other polymer systems via electrostatic, hydrogen bonding and other secondary interactions.

Figure 4 shows the nanostructures transferred using our technique on various substrates. Dense nanolines with a high aspect ratio are shown in figure 4(a). This picture indicates that the top line width is 80 nm (line spacing ∼220 nm) and the height is 400 nm. Figures 4(b) and (c) shows multilevel and complex nanopatterns on the glass substrate. In the transfer of these dense, multilevel and complex nanostructures with high aspect ratio, other techniques have some challenges to overcome, but we can easily transfer a densely nanostructured polymer film to the substrate with good fidelity. We can also transfer the nanopattern to flexible polymer films such as 3 M transparent films (figure 4(d)) because the polyelectrolyte multilayer is used as an adhesion promotion layer. These results show the effectiveness of our reported technique in dense, multilevel and complex nanopattern fabrication on various substrates.

In this report we show that dense, multilevel, and complex nanostructures such as periodic 80 nm lines with 400 nm height can be fabricated easily using a highly accurate PU mold and a polyelectrolyte multilayer as an adhesion promotion layer with high fidelity. As this technique is very simple and cheap, it can be used for the reproducible fabrication of nanostructures over areas of several square centimetres without expensive equipment. It is quite possible to extend this process to larger areas. We have also used this procedure to form nanostructures on various substrates such as Si or SiO_2 wafers, glass and flexible plastic films like 3 M transparency films—without defects—using polyelectrolyte multilayers as the adhesion promotion layer. Because the polyelectrolyte multilayer can be applied to a broad range of surfaces, many substrates can be used, making this technique applicable to a variety of fields. The new, unconventional lithographic technique presented here—when applied to a range of polymeric materials—could open the door to a variety of applications in the fields of electronic, optical and biological devices.

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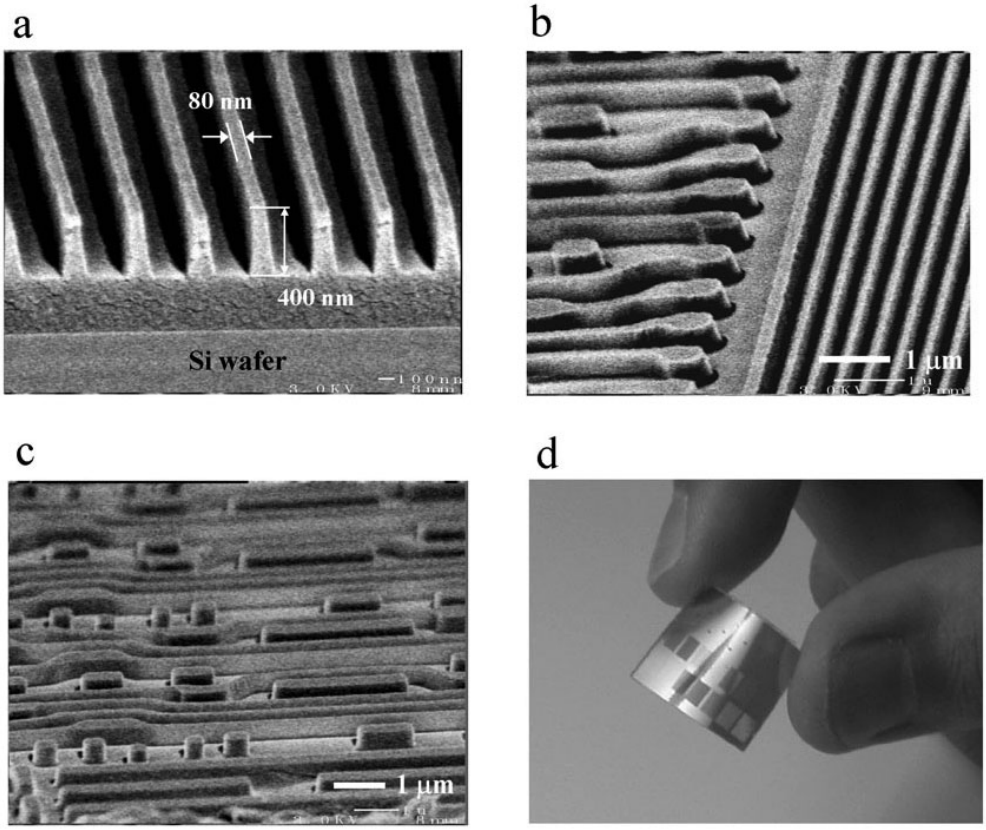

Figure 4. SEM images of replicated polymer nanopatterns on various substrates: (a) replicated polymer nanostructures on an Si wafer, including periodic nanolines with high aspect ratio (the upper top width of the periodic nanolines is 80 nm and the height of the nanolines is 400 nm); (b), (c) multilevel and complex nanostructures on a glass substrate; (d) nanostructures transferred onto polymer on flexible polymer films (3 M transparency films).

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