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Facile large-area photolithography of periodic sub-micron structures using a self-formed polymer mask

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This letter reports the methodology of a low-cost fabrication technique for producing periodic sub-micron structures over a large area, using a polymer mask. A thin film of gold/palladium or silica is deposited on a stretched polydimethylsiloxane (PDMS) substrate. Release of the tension forms a buckling sinusoidal pattern on the surface. The PDMS substrates are then used as masks in soft contact optical lithography, bypassing the need for an expensive lithographic process toward creating regular patterns on a traditional masks. Pattern transfers are conducted using an ultraviolet lamp and the fabrication of more complex periodic structures through multiple exposures is reported. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4726085]

Sub-micron periodic patterns are heavily utilized in several applications, including memory,[1] biological devices,[2,3] optoelectronics,[4–6] and solar cells based on nanostructures.[7] Although techniques capable of fabricating sub-micron features have been developed and are well understood, including electron beam lithography (EBL),[8] deep ultraviolet (UV) (Refs. 9 and 10) and interference lithography,[11,12] scanning probe microscope (SPM) lithography,[13,14] nanoimprint lithography,[14–16] and self-assembly,[17] these techniques offer their own set of prohibitive challenges. For example, EBL, deep UV lithography, and interference lithography require expensive equipment, while methods such as SPM lithography, along with EBL, have a serial write mechanism that makes large-area patterning costly and time-consuming. While nanoimprint lithography and self-assembly are relatively low cost and parallel processes, both still require an initial sub-micron patterning technique as described above, to create a master mold or masking pattern.

Another method of fabricating large area periodic sub-micron structures, namely soft contact optical lithography[18–22] has been explored recently. In this method, a polymer mask with a relief pattern is used to replace the traditional glass mask in photolithography. When light is exposed through the polymer mask onto the photoresist, there is a relative difference in light intensity between the regions in direct contact to the substrate and the raised regions that are not in contact with the substrate.[18] Due to van der Waals interactions between the polymer mask and substrate, the contact between the two is more intimate than that of a glass mask,[18] which leads to a better resolution. By controlling the exposure dose, the regions of the substrate that are in contact with the polymer mask are exposed sufficiently while the regions of the substrate that do not have enough contact are not sufficiently exposed to be developed, thus a pattern is created. However, this technique also suffers the same limitation as in nanoimprint lithography since a more expensive lithography technique (e.g., EBL) must be used to create the master mask.

In this letter, we report a low-cost approach toward creating the master mask using a polydimethylsiloxane (PDMS) polymer substrate decorated with a periodic buckling pattern on the surface.[6,23–26] Furthermore, we demonstrate the feasibility of using a simple UV lamp as the exposure source in place of a traditional mask aligner. This reduces the cost and time-limiting factors of expensive equipment and slow processes, enabling the facile fabrication of large area submicron periodic structures.

To fabricate buckled patterns atop PDMS, we use a method that has been developed for stiff buckled thin films on soft substrates. PDMS slabs of approximately 1–2 mm thickness are prepared by mixing polymer base with a curing agent at a 10:1 ratio by weight (Sylgard 184, Dow Corning) and allowing the sample to cure for 24 h at room temperature. The PDMS slabs are then stretched [Fig. 1(a)] with a strain of approximately 50%. In the stretched state, a thin layer of metal with a few nanometers thick is deposited onto the surface [Fig. 1(b)], or silica layer is formed on PDMS surface through oxygen plasma treatment. The PDMS is then relaxed and the metal layer contracts. Due to differing elastic moduli between the PDMS and metal, in addition to the fact that the metal layer itself is not stretched, the metal layer at the surface of the PDMS will buckle to form a sinusoidal pattern in order to release the total strain energy of the system. The concept of using integrated hard materials (e.g., metal layer) and soft materials (e.g., PDMS) to release the system energy has been used in many different applications, including stretchable electronics,[27–29] tunable gratings,[6] tunable lithium-ion batteries,[30] and tunable alignment of colloidal particles and viruses.[3,6]

The use of both metal and silica are tested to create the buckled surface layer. In the initial set of trials, gold and palladium (Au/Pd) are sputtered onto the pre-strained PDMS to form the patterned layer. For silica layer formation, the sample was exposed to oxygen plasma at 50 W for 30 s to form a hard silica-like layer at the surface that performs the same function as the deposited metal layer.[31,32] Using the silica formed sample, the role of the surface plasmonic effect in the exposure is explored.

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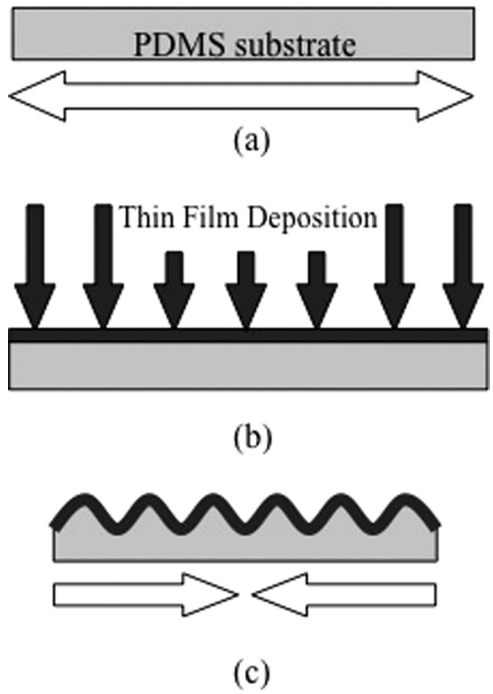

FIG. 1. Schematic of mask fabrication process. A thin sample of PDMS is stretched (a) and a few nanometers of Au/Pd is deposited or silica formed on the surface (b). Release of the tension forms the buckling pattern (c).

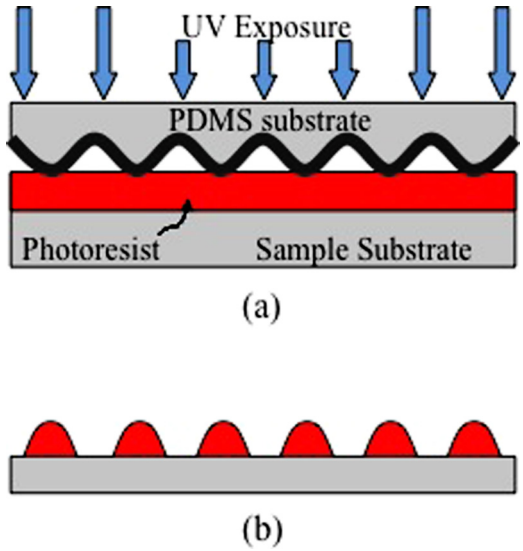

FIG. 3. Schematic of the pattern transfer process from PDMS buckled mask to photoresist-coated substrate.

As shown in an optical image in Fig. 2(a), mask of a few square centimeters was fabricated using this very simple process without sophisticated and expensive photolithography or electron beam lithography equipment. The periodicity of the pattern is approximately 1.2 μm for a sample fabricated with 90 s of Au/Pd sputtering [Fig. 2(b)]. These results are well-correlated with periodicities expected from theory.[6] It should be emphasized that this identical mask-making process can be scaled up to fabricate much larger mask sizes on the order of tens of inches if a large mechanical stretching mechanism is used.

The surface wrinkles on PDMS are then used as a soft-contact photolithographic mask in a similar manner as a traditional glass mask is used in photolithography, as shown in Fig. 3. A commercial mask aligner is not necessary for the pattern transfer because there is very little micro-scale alignment involved. A simple monochromatic 365 nm UV lamp may be used in replacement of a mask aligner, which significantly reduces the cost of fabricating the nanowell pattern.

Pattern transfer was tested on both glass and silicon substrates. Glass slides were cleaved into approximately 6.25 cm^2 squares while the silicon substrates were cleaved into approximately 1 cm^2 samples. These sample sizes are chosen with respect to the size of the masks fabricated and could be scaled up to larger sizes if a larger mask were fabricated. AZ 3312 positive photoresist was used along with hexamethyldisilazane (HMDS) as an adhesion layer.

Both glass and silicon samples were prepared by spinning HMDS as an adhesion layer at 5000 rpm followed by AZ 3312 positive photoresist also at 5000 rpm. A subsequent pre-bake was conducted on a hot plate for 30 s at 100 °C. Exposure dose calibrations were initially conducted using an EVG 620 mask aligner in order to identify the exposure dose range to create patterns using patterned PDMS mask. Subsequent exposures, including dual exposures, were used to fabricate nanopillar and nanowell arrays, and were conducted using a simple, standalone UV lamp with a central wavelength of 365 nm. The samples were placed approximately 10 cm below the lamp, at a power density of approximately 1.6 mW/cm^2. The samples were then developed in MIF 300 developer.

To start off, the sensitivity of UV exposure doses during soft-contact lithography was examined. For single exposure, the optimal exposure dose was found to be approximately 80 mJ/cm^2 on average for a PDMS mask with sputtered Au/Pd metal layer. Note, thicker metal layers can lend to slightly higher dose requirements. Exposure doses under 60 mJ/cm^2, however, are unable to break the bonds in the photoresist, leading to no patterns being transferred. Furthermore, samples

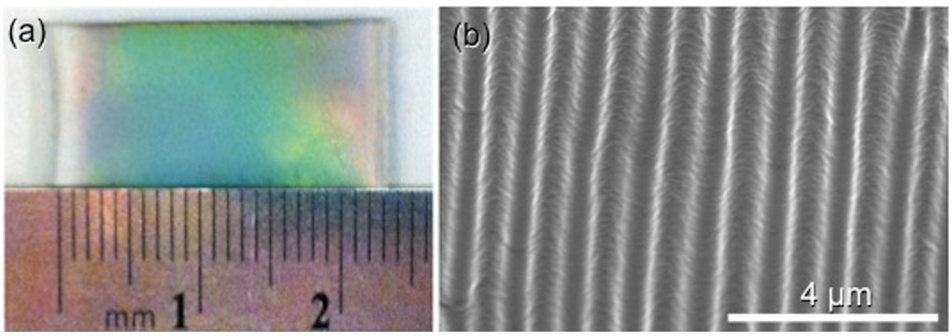

FIG. 2. (a) Optical image of PDMS mask. (b) Zoomed-in scanning electron microscope image of the sinusoidal pattern on the PDMS mask.

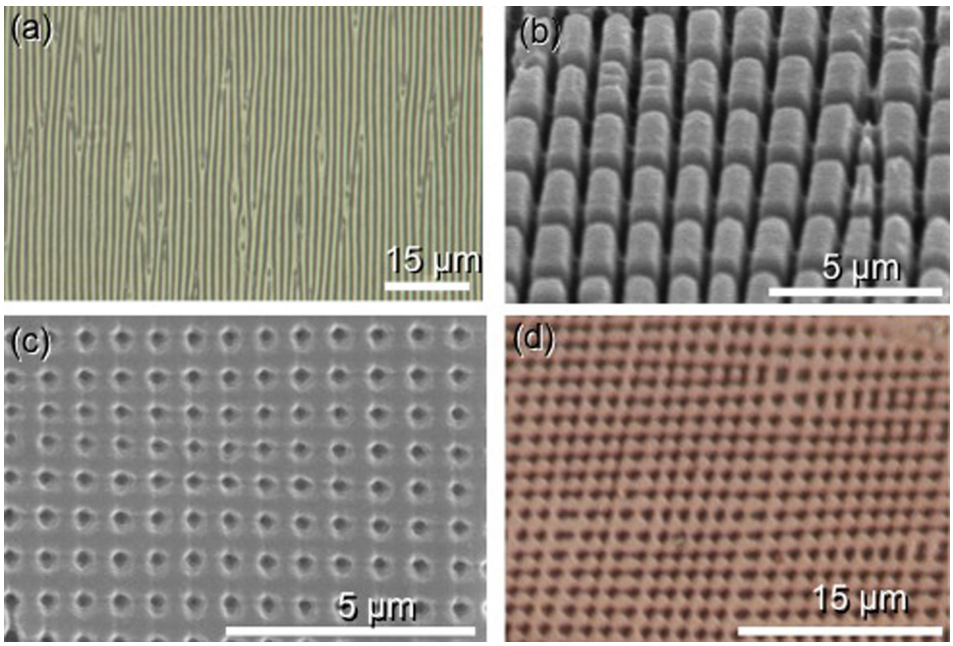

FIG. 4. Various periodic patterns can be transferred to photoresist layer through PDMS mask. (a) Image of line grating pattern transferred to glass. (b) Rectangular pillar pattern fabricated through two exposures at 60 mJ per exposure. (c) Nanowell pattern fabricated through two exposures at 40 mJ per exposure. (d) Optical image of the mask fabricated using oxygen plasma rather than Au/Pd deposition.

exposed to doses above 100 mJ/cm^2 become overexposed, which develops away all initial photoresist. Overexposure renders the areas with intimate contact with the mask and those without contact indistinguishable. Under appropriate exposure conditions, periodic structures can be transferred from PDMS mask onto the photoresist layer. Figure 4(a) shows an optical image of a periodic line pattern created on the photoresist layer through such a transfer process.

In addition to one-dimensional periodic lines that can be patterned onto photoresist layers, the use of two exposures can result in a variety of other regular two-dimensional patterns. After the initial exposure step, the mask is rotated by 90° and then the sample is again exposed. At approximately 60 mJ/cm^2 per exposure, a periodic array of rectangular pillars, as shown in scanning electron microscopy (SEM) image in Fig. 4(b), is fabricated, when using two PDMS gratings with different periodicity. The line pattern is transferred to the subtrate during both exposures. Similarly, at 40 mJ/cm^2 per exposure, an array of 2D nanowells is fabricated [Fig. 4(c)]. The exposure dose from a single exposure is unable to break the bonds in the photoresist so only points that are in direct contact with the PDMS mask during both exposures are exposed. The diameters of the wells are approximately 300 nm with a periodicity of 725 nm. These submicron features are created without using traditional high resolutuion lithography tools.

Exposure was also conducted using masks fabricated using oxygen plasma to create the thin surface buckling layer [Fig. 4(d)]. Due to the significantly more transparent nature of the mask, the total exposure dose required dropped significantly, down to approximately 30 mJ. More intimate contact between the mask and the glass and silicon substrates lead to a larger yield of areas with strongly defined patterns. Exposure trials conducted using the oxygen-plasma fabricated masks also indicate that the surface plasmonic effect is not a key mechanism toward exposure. Because the silica layer that is formed by the oxygen plasma treatment of the PDMS is insulating, therefore surface plasmonic enhancement of the electromagnetic filed in the Au/Pd layer on PDMS mask can be ruled out as the primary reason for the pattern transfer process during the UV exposure.

In conclusion, a polymer mask has been fabricated by the deposition of a Au/Pd metal layer or by the formation of a silica layer on a pre-strained sample of PDMS, removing the need for an expensive mask writing process, such as electron beam lithography. The fabrication of various submicron patterns such as line gratings, rectangular pillars, and nanowell arrays has been demonstrated by changing the number of exposures and the exposure dose. It clearly demonstrated this methodology's distinct advantage of ease of fabrication that uses of a monochromatic UV lamp instead of a commercial mask aligner, which significantly decreases the cost of fabrication, the need for expensive equipment, and the need for time-consuming processes.

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