Fabrication of Nanostructures on Curved Surfaces Using PDMS Stamp

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ABSTRACT

We report on a simple and effective process that allows direct imprinting of micro- and nanostructures on non-flat surfaces using flexible polymer stamps. Pattern imprinting was tried using a UV-curable polymer blend containing poly(propylene glycol) diacrylate, trimethylolpropane triacrylate and a photoinitiator. The UV-resist was dispensed manually on convex and concave surfaces of a glass lens and a concave surface of poly(methyl methacrylate). A thin, flexible polymer stamp was produced using polydimethylsiloxane (PDMS) by spin coating on a Si master containing micro/nanogratings. This PDMS stamp was used to conformally mold the UV resin on non-planar surfaces. With this method, we have successfully demonstrated micro- and nanostructures down to 300 nm wide gratings, as confirmed by scanning electron microscopy and atomic force microscopy. The process so developed will fill the gap in current micro- and nanofabrication technologies in that most of the technologies allow for patterning only on planar substrates.

Keywords: UV-resist, PDMS stamp, curved surface, nanostructures.

1 INTRODUTION

The ability to produce micro- and nanostructures on non-flat surfaces is of importance for many applications. Examples include flexible electronics, measuring convex secondary mirrors [1] and ultraviolet spectroscopic instruments [2]. Micro- and nanostructures patterned on sidewalls in microfluidic devices allow control over the wetting behavior of fluids flowing through the microchannel, which results in reduction in friction. In bioanalytical devices, the sidewall patterns will help prevent non-specific adsorption of biopolymers analyzed. Conventional micro- and nanofabrication techniques such as photolithography and nanoimprint lithography cannot be used to produce patterns on curved surfaces because masks or stamps used for those techniques are usually rigid. High end nanofabrication tools such as ion beam direct milling, electron beam lithography, and laser direct writing have been used to produce patterns on curved surfaces for diffractive optical elements [3-7]. Those methods are, however, too expensive and time-consuming to be implemented as flexible techniques to produce patterns on curved surfaces at low cost and with high throughput.

In this study we report on a simple and effective process that allows direct imprinting of micro- and nanostructures on non-flat surfaces. A thin polydimethylsiloxane (PDMS) stamp having micro/nanogratings was used to make pattern on the convex and concave surface of glass lens and concave surface of PMMA coated by a UV-curable polymer blend containing poly(propylene glycol) diacrylate (PPGDA), trimethylolpropane triacrylate (TMPTA) and irgacure 651. Formation of micro/nano patterns produced over curved surfaces was proved using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

2 EXPERIMENTAL PROCEDURES

2.1 Fabrication of flexible PDMS stamps

A Si master with microscale patterns was fabricated using UV-lithography while nanogratings with 300 nm period was produced via UV-interference lithography, which was followed by subsequent reactive ion etching into Si. Before coating PDMS, surface of the Si master was activated using oxygen plasma for 5 minutes and coated with a hydrophobic fluorinated silane via a vapor deposition process for 20 minutes in a home-made chemical vapor deposition chamber in order to reduce adhesion of Si master to polymer. Sylgrad 184 silicon elastomer and curing agent were purchased as a kit from Dow Corning and used without any modification. PDMS was mixed in a 10:1 mass ratio of silicon elastomer to curing agent. In order to remove air bubbles from the mixture it was vacuumed for 15 minutes. After removal of air bubbles it was spin coated on the Si master at 1500 rpm for 20 seconds. PDMS was then cured at 65° C for 4 hours and detached from the Si master in ethanol to prevent its tearing. The thickness of thin PDMS stamp is ~ 20 µm.

2.2 Patterning non-planar surfaces

Pattern imprinting was tried using a UV-curable polymer blend shown in table 1. Taking advantage of the low viscosity of the polymer, it was manually dispensed on the convex and concave surfaces of glass substrate and concave surface of PMMA. The dimensions of glass lens used as substrate are shown in figure 1. In order to make a concave surface on PMMA sheet hot embossing was employed. Using a cylindrical metallic bar having radius of 2 mm hot embossing was done at 150 °C for 5 minutes followed by demolding at 70 °C. The thin PDMS stamp was placed over the curved surface of glass or PMMA which was previously coated with the UV-resist. Gentle finger pressure was applied to the PDMS stamp to provide conformal contact with the glass substrate. The UV-resist was exposed to UV light for 10s using a UV-lamp having the intensity of 1.8 KW/cm2. The process is shown schematically in figure 2.

Monomer	**Cross-linking agent**	**Photo-initiator**
PPGDA	TMPTA	Irgacure651
70 wt%	28 wt%	2 wt%

Table1: The constituents of the UV-resist.

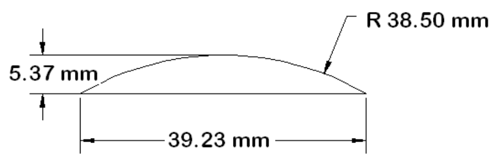

Figure 1: Schematic showing the dimensions of glass lens used as substrate.

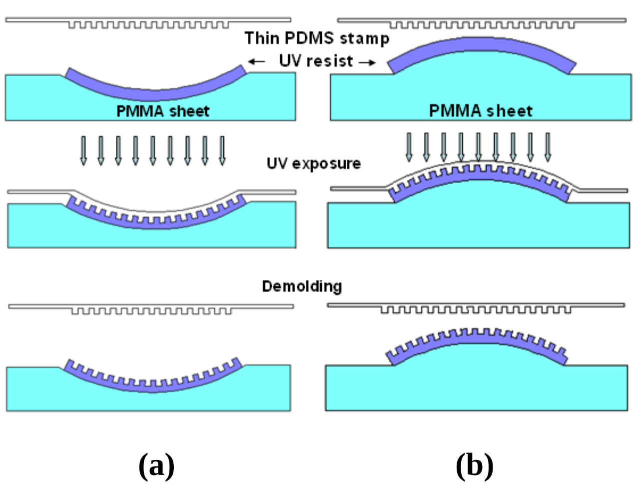

Figure 2: Schematic illustration of making patterns on (a) concave (b) convex surface using thin PDMS stamp and UV exposure.

3 RESULTS AND DISCUSSION

3.1 Large area flexible PDMS stamps

One of the key components for the process is to use flexible stamps with desired structures that can conformally mold into non-planar surfaces. Elastomeric PDMS was chosen as stamp material because it can be spin-coated on Si master easily, so that the thickness of the PDMS stamp can be easily controlled, which is a key factor for patterning curved surfaces. In addition, PDMS has low interfacial interaction with polymer substrates due to its hydrophobicity, thus it can be easily demolded without using any anti-adhesion agent [8].

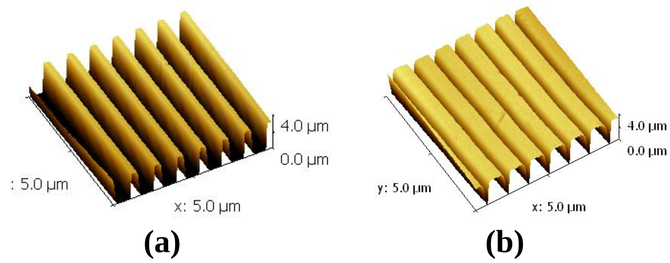

Figure 3: Atomic force micrographs of microgratings for (a) Si master and (b) PDMS stamp.

Si master was first produced using UV photolithography and RIE, which was shown in Figure 3(a). The depth of channels in the stamp was 4 µm and the width and period of channels were 3.1 and 15 µm, respectively. In order to fabricate a very flexible stamp spin coating was employed. PDMS stamps with various thicknesses were produced by changing time and speed of spin coating. A thin PDMS stamp with thickness larger than 20 µm was fabricated by directly spin coating on the stamp master. However, in the case that thiner PDMS stamps are needed, a very thin layer of PMMA was spin-coated on the Si master as a sacrifial layer prior to the PDMS coating. By dissolving this sacrifical layer in acetone, the spin coated PDMS stamp can be easily released from the Si master. Figure 3(b) shows an AFM image for a PDMS stamp that is a negative image of the Si master. The width and period of channels were 12 and 15 µm, respevtively. The depth of channels was about 4 µm. Compared to the Si master, a slight change in the dimensions of the spin-coated PDMS stamp was observed. With this spin-coating method, large area PDMS stamps up to 4 inch diameter were prepared, as shown in Figure 4.

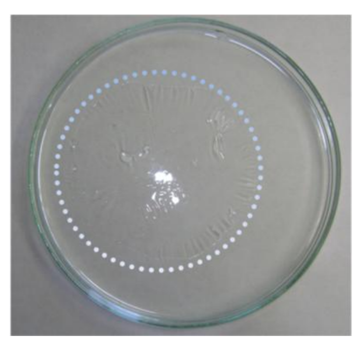

Figure 4: Photograph of a 4 inch PDMS stamp with microstructures which was released from Si master.

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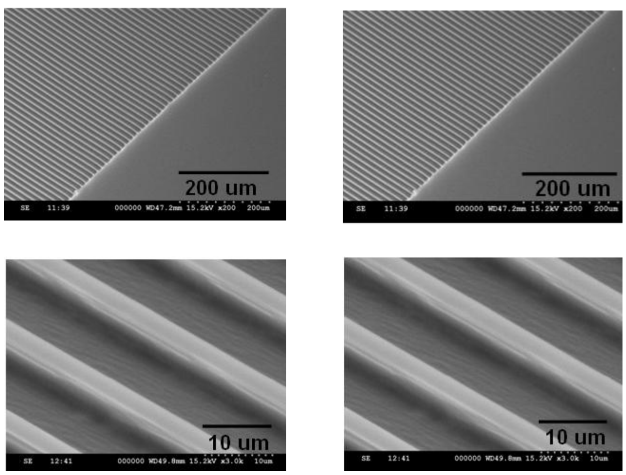
3.2 Making micro-pattern on glass lens

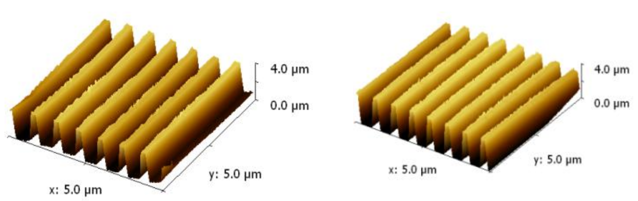
Based on the process shown in Figure 2, a thin PDMS stamp was placed over the convex or concave surface of glass lens which was previously coated by the UV-resist. Gentle finger pressure was applied to the PDMS stamp to provide conformal contact with the glass substrate. UV-resist was exposed to UV light for 10 seconds. After UV-exposure PDMS was manually released from the cured polymer. In figure 5(a) and (b) SEM images of printed pattern on concave and convex surfaces are shown respectively.



(a) **(b)**

Figure 5: SEM image of micro-pattern on (a) concave and (b) convex substrates.

Figure 6- (a) and (b) illustrate the 3-d image of micro-patterns. Using AFM the depth of micro-patterns on convex and concave surfaces was measured as 3.8µm and 3.6 respectively.



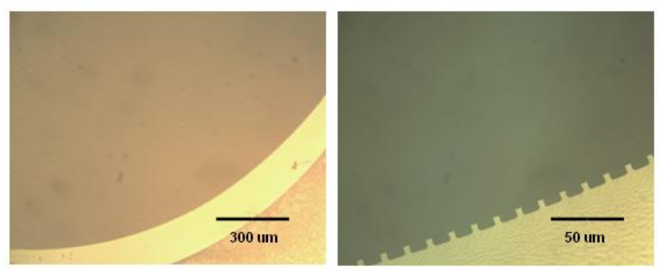
(a) **(b)**

Figure 6: 3-d images of printed patterns on (a) concave and (b) convex surfaces.

Based on SEM and AFM images it can be concluded that UV resist due to having a low viscosity can fill a considerable volume of the cavities in PDMS stamp by using a gentle finger pressure. Using pressurized gas can be a good option to improve results. Another advantage of using UV resist for patterning is short processing time which takes just 10 seconds. Also there is no need to use high pressure or temperature and stamp will not be affected by the process condition. Also, due to the low interfacial interaction of PDMS with cured UV-resist and its high elasticity, a clean separation of thin PDMS stamp from cured polymer was achieved without using any anti-adhesive agent.

3.3 Making micro-pattern on curved surface of PMMA.

Using a cylindrical metallic bar having radius of 2 mm hot embossing was done at 150 °C for 5 minutes followed by demolding at 70 °C. The thin PDMS stamp was placed over the curved surface of PMMA sheet which was previously coated with the UV-resist. After UV exposure the PDMS stamp was demoded manually. In figure 7 cross section of printed micro-pattern on the concave surface of PMMA is demonstrated. It was found that as radius of curved surface reduces it will be more difficult to keep PDMS stamp in contact with the substrate. We are currently investigating the dimensional limit of radius of curved surface in the process. Also, using a transparent fixture providing a conformal contact of PDMS stamp with substrate for low radius curved surfaces can be considered.



(a) **(b)**

Figure 7: Cross section of printed micro-pattern on the concave surface of PMMA

3.4 Making nano-pattern on glass lens

The process shown in Figure 2 and explained in 3.2 was employed in order to investigate the applicability of the method to nanoscale patterning. For that, a Si master with gratings of 300 nm width and 210 nm depth was used to produce a PDMS stamp via spin-coating. The PDMS stamp was used to make pattern on the concave and convex glass lenses. In figure 8 the photograph of printed pattern is shown. Figure 9 shows AFM images for the Si master, PDMS stamp, and printed UV-resist on curved surface with nanoscale gratings fabricated using the process shown in figure 2. The measured depth of PDMS stamp and printed UV-resist on both concave and convex substrates were 220 and 150 nm respectively. A period grating pattern is clearly observed in the UV-resist printed on curved surface with almost similar depth to that of the Si master and PDMS stamp. This indicates that the proposed method is easily extended to 3-D patterning of nanostructures. However, it seems employing gas pressure during molding process can improve the results.

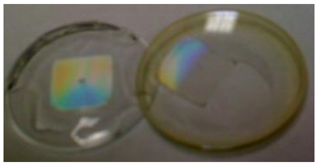


Figure 8: Photograph of nano-pattern printed on convex and concave surface.

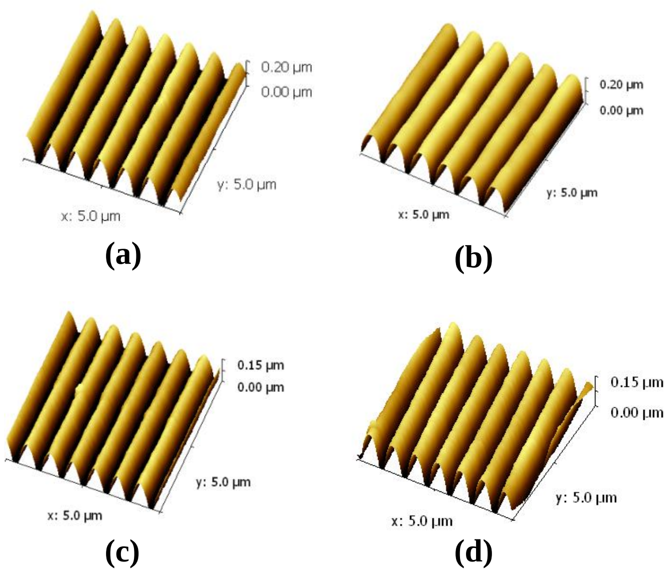


Figure 9- 3: d image of (a) Si master (b) PDMS stamp printed pattern on (c) concave (d) convex surfaces.

4 CONCLUSIONS

We have developed a simple technique to produce micro- and nanostructures on non-flat surfaces using a thin, flexible stamp and a UV-resist. The results showed that a thin PDMS with desired structures is suitable as a stamp to make such 3-D structures. Thin PDMS stamp can cover the curved surface coated with UV-resist and its cavities can be almost filled by the UV-resist when a gentle finger pressure is applied. After curing UV-resist PDMS can be easily peeled off the substrate without using any anti-adhesive layer. The process so developed will fill the gap in current micro- and nanofabrication technologies in that most technologies allows for patterning on planar substrates only.

Acknowledgments

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