Fabrication of diffractive optical elements on 3-D curved surfaces by capillary force lithography

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Abstract: We demonstrate the fabrication of diffractive optical elements (DOEs) on 3-Dimensional curved surfaces by capillary force lithography (CFL). Curved gratings with a period of 20μm and 820nm have been successfully fabricated in polymer on concave surfaces by CFL. The experiment results indicate that the capillary force lithography is an effective method to replicate DOEs on curved surfaces with a very high fidelity and a relatively fast speed. In addition, we found that the growth rate of the polymer in the sub-microfabrication is much faster and the step height is much closer to the master than that in the microfabrication for CFL, which makes CFL more attractive in the fabrication of DOEs with a sub-microscale or even nanoscale feature size than a microscale feature size.

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1. Introduction

The ability to fabricate the micro/nano-structures on 3-D curved surfaces allows to produce many useful devices such as electronic eye camera [1] and artificial compound eyes [2]. Over the past few years, great efforts have been made to develop the micro/nano patterning method on arbitrary 3-dimensional curved surfaces. Methods including laser direct writing lithography technique [3,4], decal transfer lithography [5,6] and others [7] have been established to fulfill this purpose. Xie et al demonstrated the fabrication of DOE on 3-D curved surfaces by laser direct writing method and the fabricated DOE has been successfully applied for the aspherical surface profile test [8,9]. However, the laser direct writing method requires a set of expensive equipment. In addition, the fabrication process by laser direct writing is very time consuming and thus not cost-effective. Decal transfer lithography is a modified process of soft lithography [6,10], which uses a planar PDMS stamp to form patterns on curved surfaces and therefore the deviation to the original shape is unavoidable to some extent. In addition, the process for decal transfer lithography is very complicated as well.

Capillary force lithography (CFL) [11,12] utilized the capillary-filling phenomenon of a polymeric melt into a cavity to pattern the polymer film coated on a substrate. In fact, CFL method is a combination of imprint lithography [13,14] and soft lithography [10]. As a result, by inheriting the advantages of both methods, CFL has the ability to pattern structures at nanoscale as well as in a simple process. As far as we know, the capillary had been used for the first time in a method called micromolding in capillaries [15] in 1995. However, it was not until 2001 that CFL was proposed [11] formally. From then on, CFL was extensively studied. In order to obtain better pattern qualities, some modified CFL methods, i.e. pressure-assisted CFL (PA-CFL) [16] and solvent-assisted CFL (SA-CFL) [17], have been developed as well. Capillary force lithography (CFL) possesses many attractive characteristics, such as high resolution, simple process, short cycle time, high fidelity, and the ability to pattern in a large-area and so on. It has already been applied to many new fields such as cell and tissue engineering [18] and communication engineering [19].

So far, all the studies of CFL are performed on 2D planar substrates. To our knowledge, to fabricate microstructures on curved surfaces by CFL has not been reported yet. In this paper, we demonstrate that capillary force lithography (CFL) can be employed to fabricate micro- and nano-structures on a curved surface with a high fidelity. Specifically, DOEs have been fabricated on a concave surface successfully.

2. Experiment

In our experiment, the master is a concave lens with a concentric circular grating fabricated on its surface by laser direct writing lithography technique, which had been studied intensively by our group [3,4,7,8]. The substrate has a diameter of 40 mm and a curvature radius of 49.32 mm. We use the Shipley S1813 Microposit photoresist, which is diluted with Shipley Type P Microposit thinner in a volume ratio of 2:1 (photoresist: thinner). The photoresist is spin-coated onto the concave substrate with a spin speed of 1400rpm for 40s. A film thickness of approximately 0.7μm has been obtained. Figure.1 shows the master with micro-concentric circular structures fabricated on its 3-D curved surface by laser direct writing.

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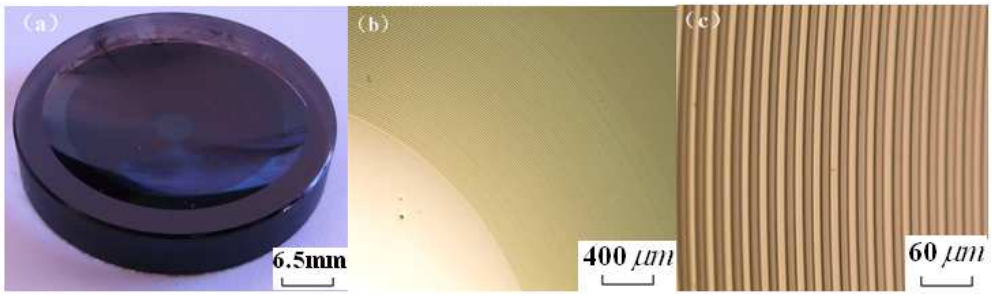

Fig. 1. (a) A panorama of the master with micro-concentric circular grating fabricated on its 3-D curved surface by laser direct writing and (b) Image of the 30 × magnified image of the grating under microscope and (c)Image of the 200 × magnified image of the grating.

A schematic diagram of fabrication of micro/nano-structures on a curved surface by capillary force lithography (CFL) is shown in Fig. 2. 3D curved master molds and glass substrates with curvature radii of 49.32mm and 196mm have been used in CFL experiments. Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) is used to fabricate the elastomeric molds. The PDMS mold is prepared by casting the PDMS liquid polymer (prepared by mixing PDMS monomer with curing agent with a volume ratio of 10 to 1) on the master firstly, then allow PDMS polymer to cure at a temperature of 65$^{\circ}C$ for 2hrs, and finally the PDMS mold is peeled off carefully from the master after fully curing and cooling down to room temperature.

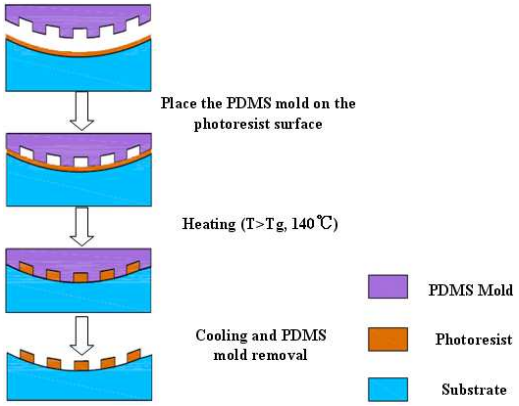

Fig. 2. A schematic diagram of fabrication of micro/nano-structures on a curved surface by CFL.

The process of the fabrication of micro/nano-structures on 3-D curved surfaces by capillary force lithography (CFL) is described as follows. Firstly, a glass substrate with a concave surface is cleaned by ultrasonic treatment in isopropanol, acetone and ethanol for 5 min each and then dried by nitrogen blow. Next spin-coating method is used to form a thin photoresist film with a thickness of about 700nm on substrate. Then, the PDMS mold was put onto the photoresist film surface. To make sure the conformal and intimate contact between PDMS mold and the photoresist film, a slight pressure is applied onto the PDMS mold. In order to remove the air trapped between the mold and the film surface, the whole setup is heated up gradually on a hot plate with the temperature rising from the room temperature to the glass transition temperature of the photoresist at a step of 15$^{\circ}C$ and lasts for 10 min for every temperature node. When temperature is at above the glass transition temperature, capillarity forces the photoresist polymeric melt into the void space of the channels or cavities between the PDMS mold and the photoresist film. After cooling to the room temperature, the PDMS mold is removed carefully and the formed micro/nano-structures are retained on the surface of the substrate.

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3. Results and discussions

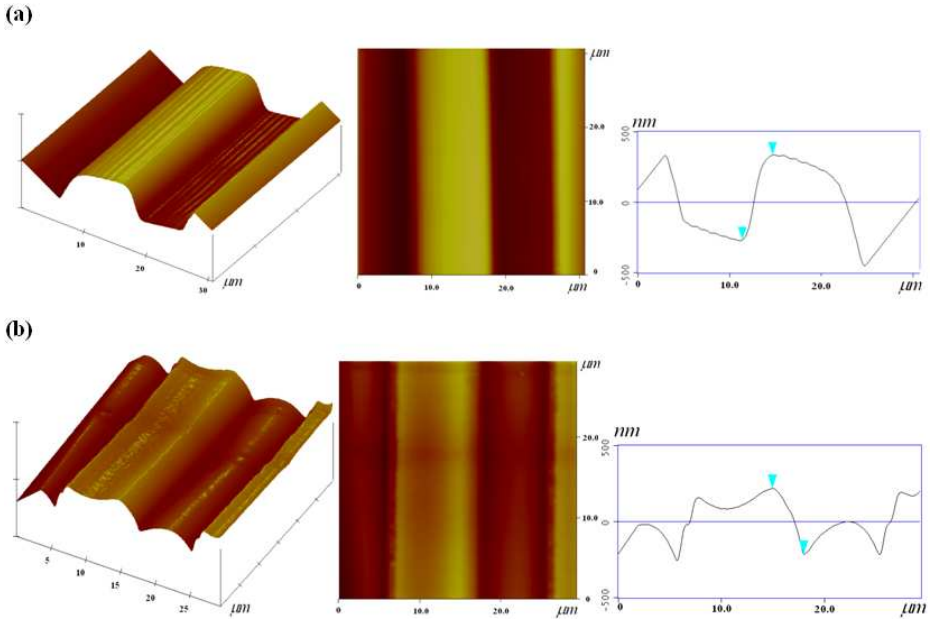

Fig. 3. (a) AFM measured 3D and 2D surface profiles of the master shown in Fig. 1; (b) 3D and 2D surface profiles of the fabricated microstructure measured by AFM.

Figure 3(a) shows the 3-D and 2-D surface profiles of the DOE on the surface of the master shown in Fig. 1. The DOE is a concentric circular grating fabricated by laser direct writing method. The period of the grating is 20μm and the bottom width of the groove is about 7.5μm measured by atomic force microscope (AFM). The cross section image shows that the height of the master is approximately 700nm. Figure 3(b) shows the 3-D and 2-D surface profiles of the DOE fabricated by capillary force lithography (CFL) process described above. The sample was annealed at 140°C for 21hours without being disturbed and characterized by AFM. It should be noted that it is difficult to measure the micro/nano-structures on a curved surface by AFM due to the probe cannot easily approach and touch the surface of the micro/nano-structures on a curved substrate. To fulfill this purpose, the sample needs to be put in the right position to ease the probing process. As can be seen from Fig. 3(b), the fabricated microstructure has a meniscus shape which is the typical sign of the capillarity. The step height measured by AFM is 410 ± 7nm, the period is 19.74 ± 0.22μm and the groove width is 7.34 ± 0.23μm. Comparing with the master, the grating microstructure has been replicated with a very high fidelity except for that the step height is smaller than that of the master. However, the step height can be further increased by extending the annealing time.

Figure 4 displays the step height versus the annealing time. As can be seen from the figure, the step height can be increased to 454nm after a 48-hour annealing, which is about 65% of the master. In addition, one can see that the step height increases rapidly at the first 2-hour annealing and can reach nearly half of that of the master. However, after 2hours, the step height increases rather slowly and the increment of the step height has a quasi linear relation with the annealing time as shown by the curve in Fig. 4, Thus, we can predict that it will take about 132 hours for the step height to reach the full height of the master by a linear fitting with the last four values. In fact, it appears that the curve in Fig. 4 is saturating, and is quite likely that it will take even longer than 132 hours to achieve the same step height with the master, which will make the process rather time-consuming and not a practical fabrication method any more. The mechanism that the step height increases during the annealing process in capillary force lithography can be explained as follows. During the lithography process, the

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capillary rise of the polymeric melt will occupy the void space of the microcavity and therefore makes the pressure of the trapped air rise, and then the increased air pressure will stop the capillary rise of polymeric melt. Apparently, assuming that the trapped air cannot permeate out from the microcavity, the capillary rise of the polymeric melt will stop at some time point when the force balance on the polymer surface reached. However, since the PDMS material is permeable, the trapped air will permeate out from the microcavity gradually during the annealing process, and therefore allows the capillary rise of the polymeric melt continues to happen and the height of the fabricated pattern can be increased. Based on above mechanism, the increase rate of the fabricated pattern at the very beginning of the capillary rise of the polymeric melt should be very high due to the trapped air pressure is relatively low at this stage. As the polymer melt continues occupy the void space of the microcavity, the pressure of the trapped air will rapidly increase due to the permeable rate is not high enough for the trapped air to escape out quickly. As a result, the dynamic equilibrium reaches and the increase of the fabricated pattern stops. From that time point on, the increase rate of the fabricated pattern will depend on how fast the trapped air can permeate out of the microcavity. Assuming the permeable rate of the mold is constant, and then the increase rate of the fabricated pattern should be proportional to the annealing time. Thus, it should be reasonable to take a linear fit with the last four data sets to predict the time taken for the fabricated pattern to achieve the same height with the mold. Above explanation about the process mechanism agrees well with the phenomenon shown in Fig. 4.

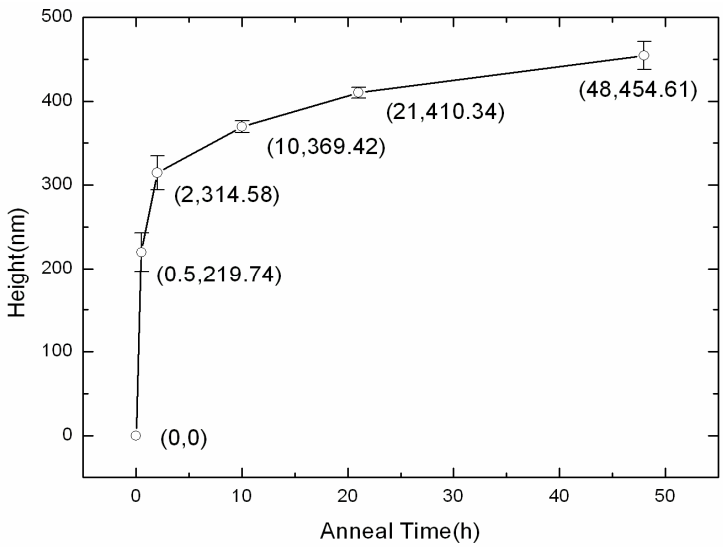

Fig. 4. The step height versus the annealing time in the process of fabricating microstructures by CFL.

Table 1. Measured optical transmission of the fabricated DOE shown in Fig. 3

Diffraction order	3	2	1	0	−1	−2	−3
Measured diffraction efficiency	0.0231	0.0641	0.0974	0.3538	0.0897	0.0513	0.0205
Calculated diffraction efficiency	0.0046	0.0517	0.3010	0.1475	0.3010	0.0517	0.0046

The fabricated DOE on curved substrate has been optically tested by using a He-Ne laser with a beam diameter of about 1.5mm. The grating shows a strong diffractive effect and the transmission for different diffraction orders is listed in Table.1. Since there is no model for calculation of the diffraction efficiency of the diffractive grating on a curved surface, we calculate the diffraction efficiency for a planar grating with the same period and step height by employing the rigorous coupled wave analysis method. The theoretical results are shown in Table.1 as well. Comparing the experimental and the theoretical results, a large deviation on

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the diffraction efficiency can be observed. The reason for this large discrepancy is obvious and can be explained from two aspects. On one side, a simulation model based on 2-D planar substrate but not on 3-D curved substrate has been used, which will surely cause a big difference on the simulation results. On the other side, in the simulation, a binary grating model is used. However, as can be seen from Fig. 3 that the fabricated diffractive grating does not have a perfect binary surface profile and there is obvious curvature on the top and the base. As a consequence, the simulation result has a great discrepancy from the experimental testing result. In order to simulate the diffractive grating on 3-D curved substrates in a more accurate way, a new diffractive model based on 3-D curved substrates needs to be developed.

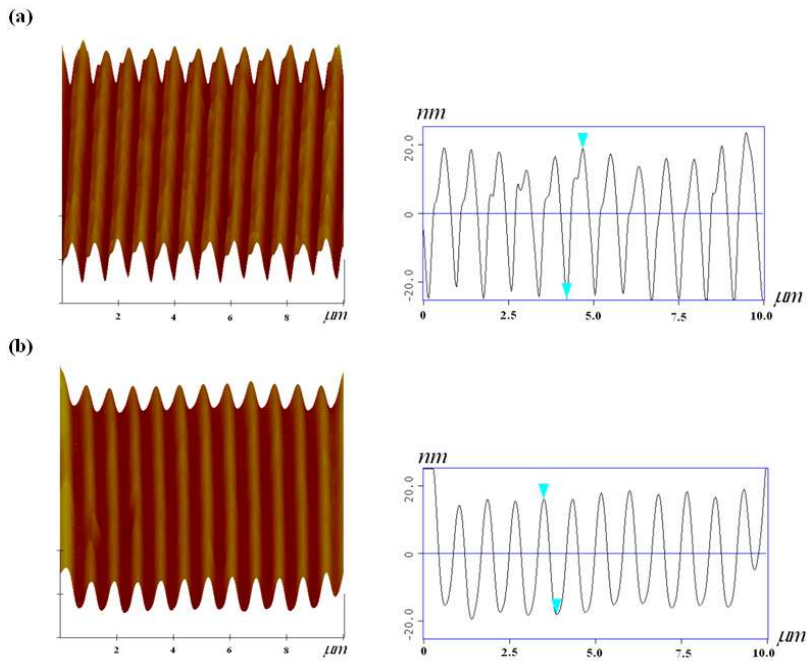

Fig. 5. (a) AFM image of the original nano-grating structures (b) AFM image of the sample fabricated by CFL.

We have also demonstrated the fabrication of DOE with sub-microscale feature size on a curved substrate by CFL. The master in this case is a diffraction grating with a concave surface profile. The diameter of the master is 50mm and the radius of curvature of its concave surface is 196mm. As shown in Fig. 5(a), the grating on the master surface has a period of 820nm and a step height of 44nm. After the CFL process, annealing at $140^{\circ}C$ for 1 hour, a concave sample grating with a period of 820 ± 12nm and a step height of 34 ± 5nm has been obtained. It can be seen from Fig. 5 (b) that the surface of the nano-structures fabricated by CFL is much more smooth and uniform than that of the master. That is to say, some defects with a fine feature size on the top of the grating surface in the master mold have not been well replicated in the polymer. However, we take this as an advantage of this method. In fact, optical elements like DOEs prefer to have a smooth surface with very low surface roughness and thus to enhance the performance of the optical elements. Again, the step height of the grating fabricated by CFL is smaller than that of the master. However, this time the step height has increased to 78% of the master only after 1hour annealing time. Comparing with the CFL process in microscale case, the growth rate here is much faster, and the step height is much closer to the master, which makes CFL more attractive in the fabrication of sub-micron or even nanostructures on the curved surface.

The increase of the step height during the annealing process for the fabrication of sub-micron structures shows a similar phenomenon with that of the microscale fabrication case. Figure 6 shows the relation between the step height and the annealing time. As can be seen,

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the height increases very fast at the very beginning and can reach nearly 70% of the full height after a half an hour annealing process. However, the height will increase slowly and only reach 83% after a two hours annealing process. This abrupt change of the growth rate of the height means the force balance between the trapped air pressure and the capillary force must have reached and therefore stops and slows down the capillary rise of the polymeric melt. The further growth rate of the polymeric pattern will greatly depend on the permeable rate of the trapped air.

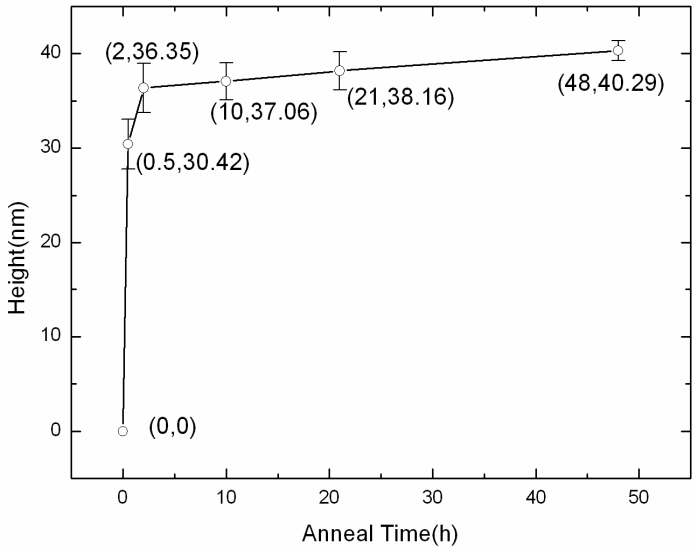

Fig. 6. The relationship between the height of the sub-microsized pattern and the annealing time.

Comparing our results with other literatures, it is found that generally our conclusions agree with others. For instance, we conclude that the polymeric structure growth rate is inversely proportional to the size of the microcavity or the channel width, which can be well explained by the modified Poiseuille model reported in reference [20]. However, comparing with the capillary force lithography in planar substrate case, it is found in our case that the polymer seems never to be able to fill up the microcavities even after an extremely long annealing time. The reason for this issue is complex and a number of factors including the viscosity, the surface tension, the initial film thickness of the polymer and others. More importantly, the 3-D curved surface profile will definitely affect the force balance during the capillary rise of the polymer as well.

Talking about the resolution of the process, it is only because that the master mold with a smaller feature size is not available for us at this moment so that we could not demonstrate the fabrication of DOE with a much higher resolution. But we do believe this process should have a higher resolution down to nanoscale, which shall be tested in our future work.

Consequently, further work needs to be done to optimize and fully understand the process for the successful application of capillary force lithography on 3-D curved surfaces. In future work, better film deposition method such as spray coating or dip coating method should be tried to achieve a more uniform film on 3-D curved surfaces. In addition, nanoscale fabrication experiments should be tested to explore the resolution limit of this process.

4. Conclusions

In summary, it has been shown that the capillary force lithography (CFL) is an effective technique for fabricating micro and nano-structures on curved surfaces. DOEs with feature size in micron and sub-micron scale have been successfully fabricated on the surface of a concave lens by CFL in a relatively short processing time. In addition, for sub-microscale

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fabrication, the surface roughness is much smaller for the fabricated DOEs by CFL than that of the master. All these advantages make the method a very promising technology for the fabrication of DOEs on 3-D curved surfaces. However, it is worth to point out that further work needs to be done to optimize and fully understand the process so that it can be successfully applied for the fabrication of nanostructures on 3-D curved surfaces.

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