

Nanopatterning planar and non-planar mold surfaces for polymers replication

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ABSTRACT

Nanostructured surfaces offer advanced functionality, such as stunning structural colors, antireflective, self-cleaning or antifogging effect. Polymer injection molding provides a cost effective method to fabricate plastic objects with complex shapes and is known to replicate nanosized details of the mold surface. It is however difficult to pattern the mold, in particular if non-planar surface is needed. We show a novel method using nanopatterned nickel foils for a room temperature nanoimprinting into hydrogen silsesquioxane (HSQ) spray-coated films deposited on freeform surfaces. Due to the high viscosity of HSQ, pressures up to 800 bar need to be used. We have been able to imprint the 426 nm period nanopattern onto conical and spherical substrates with a radius of curvature as low as 500 μm , using a specially developed high pressure hydrostatic imprinting device. Pattern distortions, resulting from a contact between the intrinsically planar foil and double-curved substrate have been found and measured as a function of a radial distance to the apex of spherical protrusion. This way, a feasible method to create freeform molds with nanopatterned surface is demonstrated. This facilitates new options for production of affordable polymer articles with novel surface functionalities.

Keywords: nanoimprint, non-planar, HSQ, injection molding, functional surfaces

1 INTRODUCTION

Nano- and micro-structured surfaces, which give an additional surface functionality, are abundant in nature. With a half billion years of evolution, the structures and functions of the surface are almost perfect for helping natural creatures to evade, hide, survive, live and prosper. The artificial man-made structures can often reach sizes below the minimum sizes of natural nanostructures, and we have been able to create even completely new structures,

unseen in nature, such as single walled carbon nanotubes or quantum dots. Unfortunately, the vast majority of those man-made nanopatterns and nano-objects have been created on planar substrates. Polymer injection molding is one of the most widespread fabrication process, capable of affordable production of plastic parts with a complex shapes and is known to replicate even the smallest features on the surface of the used mold cavity [1].

If we want to access the full potential, we need to be able to structure also non-planar surfaces, such as the mold cavities for polymer replication. Due to obvious limits of projection methods, nanoimprinting [2], embossing or pattern transfer where a stamp, an imprint tool, intrinsically planar is brought in contact with a freeform, non-planar, substrate is our method of choice. There are previous reports of nanopattern transfer into the curved PMMA polymer substrate (by Choi *et al.* [3] and recently by Farshchian *et al.* [4,5]) but for the use as a molding tool, in repeated contact with an injected polymer melt at high pressures and temperatures, one needs different resist.

The hydrogen silsesquioxane (HSQ) can be imprinted, [6-8] and is sufficiently hard and tough to be used as an injection mold cavity insert surface. Another interesting method is employing soft PDMS stamp to deposit HSQ [9].

2 MATERIALS AND METHODS

In order to imprint into the HSQ film, we need to prepare robust stamp, in our case we used nanopatterned nickel foil, which is created in process shown in the Figure 1. Briefly, we used a conventional photoresist (AZ5214E) spin-coated on a glass wafer (to avoid the resist/substrate backreflections) with the 1 mm thick layer of red-orange dye loaded polymer poured on the backside (to limit the wafer/air backreflections). Wafer is then exposed in the interference lithography system, using a He-Cd laser operating at 442 nm in continuous wave mode. The substrate was exposed (twice if a cross-grating pattern is needed). The resist with recorded nanopattern was then

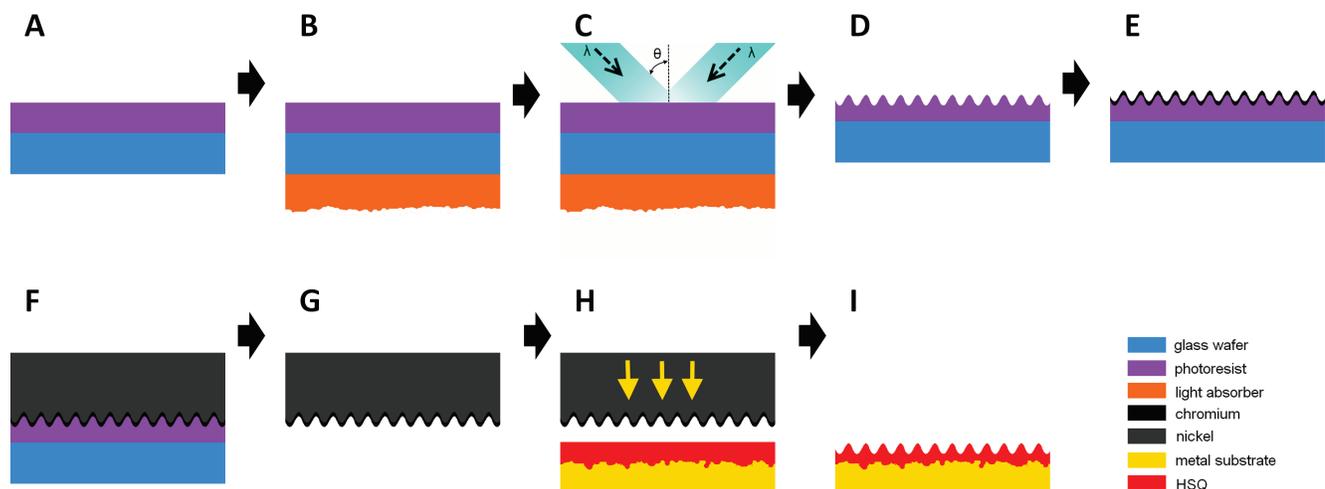


Figure 1. The process flow to prepare the nanopatterned nickel foil for an imprinting into an HSQ film. (A) Glass wafer is spin-coated with 1.5 μm of AZ5214E resist. (B) a polymer backside absorber is deposited. (C) Interference lithography exposure(s) to record fringe pattern (D) Photoresist development, where a corrugated phase grating is formed. (E) e-beam deposition of chromium seed layer. (F) Nickel electroplating step, 25-350 μm . (G) Separation, cleaning and FDTS coating of Ni foil. (H) high pressure room temperature nanoimprinting of Ni into the HSQ layer on planar or non-planar surfaces, where the substrate is metallic mold insert.

developed using the AZ351 developer in water. An e-beam evaporation process to deposit a thin, 60 nm layer of chromium metal was performed after the wafer with resist was spin-dried. This layer is then used in the subsequent electroplating step, where the Ni layer of desired thickness is grown. Surprisingly, the glass wafer self-separates from the nickel film with resist. This nickel foil is then carefully cleaned with solvents to eliminate the remaining photoresist, blow-dried and coated with an adhesion reducing layer of FDTS as described in [10].

The non-planar substrates were rapid solidified alloy RSA 6061 aluminum mold insert, with a diameter of 33 mm, prepared by a turning operation. The tested protrusions are approx. 200 μm high spherical caps and cones.

HSQ films (FOx-16) are applied using a spray-coating technique with an ultrasonic nozzle. An MIBK diluted resist forms a mist which is then forced to the substrate using a carrier gas stream. Unlike spin-coating, this method is fully compatible with freeform surfaces. Films are cca 1.3 μm thick. Deposited films are then placed in a chamber with solvent (MIBK) vapor to for 30-180 minutes to soften them and to melt away deposited semi-dry particles.

Imprinting is carried out in a specially developed device, shown in the Figure 2. It is an enclosure, with the disc-shaped cavity, filled with the cured PDMS. Operation is simple, the piston A is pushed down to the cavity B, filled with PDMS, while the device (C and D) is held together by a set of bolts.

Imprinted films are then cured at 400 $^{\circ}\text{C}$ to harden and form the final insert, usable for injection molding.

They are characterized using the SEM (FEI NOVA 600 NanoSEM) operated at low vacuum mode to prevent charging. For the pattern distortion evaluation, strictly top-

view was used, a zero stage tilt, a zero beam tilt. The position was changed strictly by the stage movement, going from the apex of double-curved protrusion in steps to the alternating sides, where the micrograph was recorded and pattern period was analyzed using 10-25 periods.

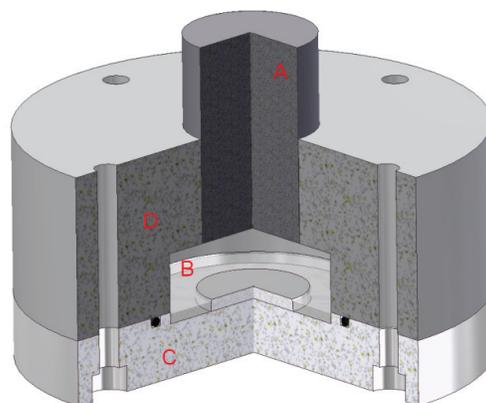


Figure 2. Dedicated high pressure embossing device.

3 RESULTS AND DISCUSSION

The figure 3 on next page shows photographs and profiles of nanopatterned non-planar surfaces after the hydrostatic high pressure imprinting with Ni foil into spray-coated HSQ films on aluminum substrates. The pressure needed to imprint the pattern is 600-800 bar. One can see, that multiple geometries have been successfully tested, including the challenging concave spherical surface. Occasionally, we have been able to observe minor issues with particles in the HSQ film. Both the diffraction and the

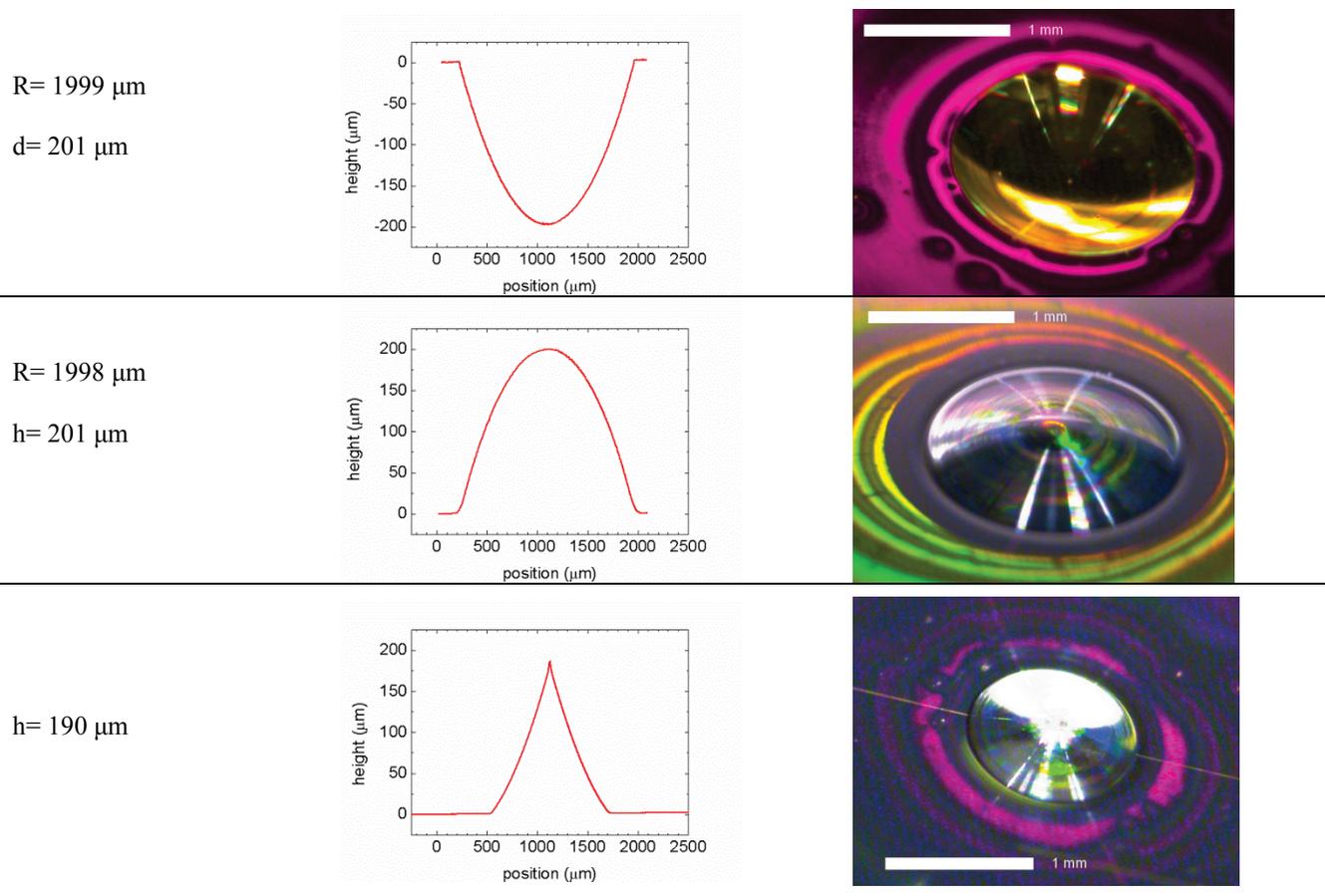


Figure 3. The right column shows some of nanopatterned double curved HSQ surfaces on the aluminum substrates. Note the diffraction on both curved and planar areas. The left column shows the actual measured profiles using a stylus profilometer.

pattern depth are reduced in a vicinity of those particles. Their source is not clear, as the process is carried out in a cleanroom, but since particles often emerge even prior to the imprinting, we can speculate that they come from the spray-coating process itself. Now, as we established a method to prepare double-curved nanopatterned surfaces

we can proceed to the measurement of pattern distortion. We measured pattern period at various position to assess the strain of the planar foil in a contact with a double-curved surface. A few examples of those measurements are shown in Figure 4, where you can see patterns on the spherical and conical surfaces.

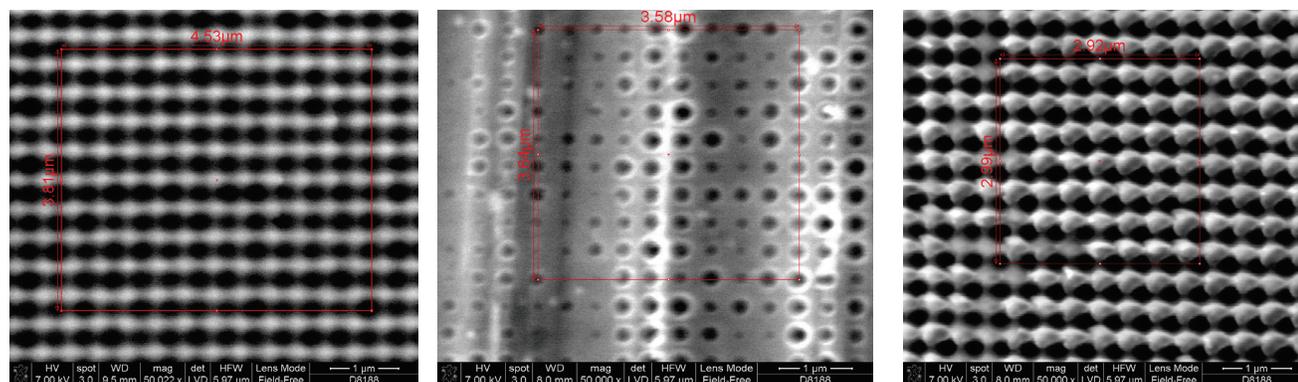


Figure 4. The SEM micrographs, from left: Pattern on the spherical surface with $R=1000 \mu\text{m}$, at $80 \mu\text{m}$ off the apex. Next: The position at $180 \mu\text{m}$ off the apex of a cone, note the machining marks and the pattern copied over. Next: The pattern in the center of a conical surface.

The plot of the pattern period, as a function of radial distance, for one selected surface, is shown in figure 5.

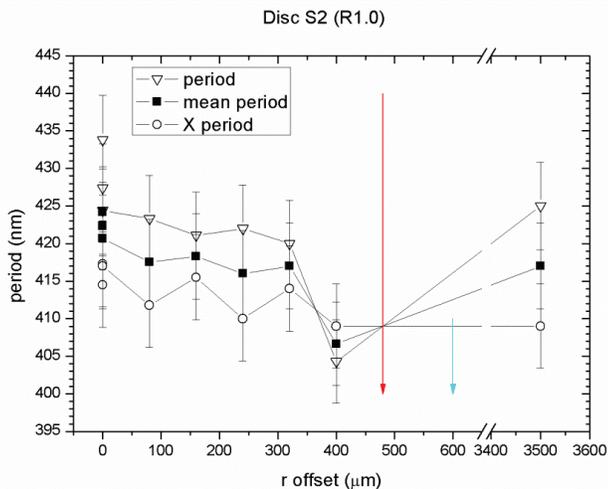


Figure 5. The observed pattern period as a function of radial distance, for a spherical protrusion with the radius of 1 mm. The red mark shows nanoimprint limit, boundary, behind which the pattern is no longer replicated. The blue marker shows a total structure radius, behind this line is the surface no longer curved but flat.

Note that the observed period is not true period, but the projection, as we are in a top-view mode. We need to apply geometrical mapping to correct for the projection error in order to obtain the period in the corresponding tangential planes for each observation. This can be done and result can serve as tool to design pre-distorted pattern on a nickel master.

4 CONCLUSION

In this work we demonstrated a method to form nanopattern on highly curved surfaces, such as cones and concave and convex spherical caps with a depth of 200 μm and a radius of curvature as low as 500 μm. Pattern was nanoimprinted using a Ni foil as a master and an HSQ film deposited by spray coating on freeform substrates from aluminum. Due to the high viscosity of HSQ films, hydrostatic pressure of up to 800 bars was used. Prepared nanopatterned surfaces can be used as injection mold inserts, and when more advanced patterns are prepared, we can fabricate large amounts of polymer parts with functional surfaces

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