Injection molded superhydrophobic surfaces based on microlithography and black silicon processing

Emil Søgaard*, Kristian Smistrup**, Nis Korsgaard Andersen* and Rafael Taboryski*

* Department of Micro- and Nanotechnology, Technical University of Denmark, DTU Nanotech, Building 345B, DK-2800 Kongens Lyngby Denmark,
emil.sogaard@nanotech.dtu.dk, Mobile +45 21444236.
** NIL Technology, Diplomvej 381, DK-2800 Kongens Lyngby, Denmark.

ABSTRACT

This work is concerned with the design, development, and testing of nanostructured polymer surfaces with self-cleaning properties that can be manufactured by injection molding. In particular, the superimposed micro- and nanometer length scales of the so-called Lotus effect were investigated in detail with an engineering perspective on choice of materials and manufacturability by injection molding. Microscope slides with superhydrophobic properties were succesfully fabricated. Preliminary results indicate a contact angle increase from 95° for the unstructured polymer to a maximum 150°. The lowest drop roll off angles observed were in the range 1° to 5°.

Keywords: injection molding, black silicon, super-hydrophobic, polymer, surface functionalization

1 INTRODUCTION

Micro- and nanostructuring can be used to functionalize surfaces to obtain super hydrophobicity and self-cleaning properties [1].Traditionally surfaces are functionalized for such properties with chemical or nanoparticle coatings. However, chemical and nanoparticle surface coatingss add potentially hazardous chemicals or nanoparticles to the products, and are often expensive.might be toxic and therefore, their use is limited. Furthermore, the production is time consuming and often is expensive.

The Lotus effect [2] is used as inspiration for the fabrication of injection molded polymer surfaces with self-cleaning properties. Self-cleaning surface properties are often obtained by having hierarchical nano- and microstructures[3]. Injection molded hierarchical nano- and microstructures from thin aluminum foils have been demonstrated by e.g. Puukilainen et al [4]. Here, we present a new method for the fabrication of tool inserts with hierarchical nano- and microstructures (Figure 1). The method is based on a UV LIGA [5] process combined with a black silicon etch. FDTS coated silicon microstructures with black silicon are known to be superhydrophobic [6].

The advantage of our method is the industrial manufacturability associated with the LIGA process and injection molding combinded the superior superhydrophic properties due to the hierarchical micro and nanostructures. Surfaces with self-cleaning properties that imitate, e.g. the lotus flower, are of relevance for the medical equipment and food industries. Food containers can be designed so they can be completely emptied leading to less or no waste.

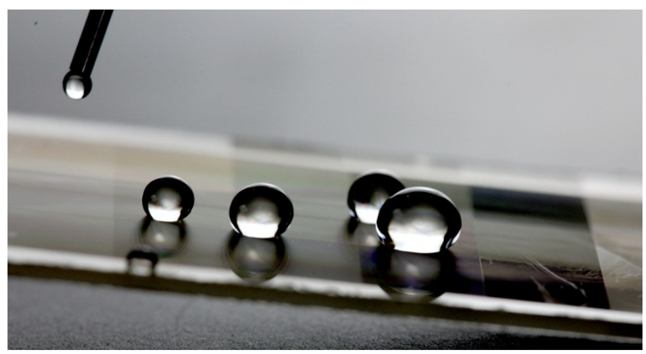

Figure 1: Drops on slightly tilted surface, excellent superhydrophobic properties.

2 METHODS

Test areas with microstructures in the form of circular pillars were fabricated with standard photolithography on clean Si wafers. The entire fabrication process is shown in Figure 2. A 1 µm photoresist layer was spin coated on to the silicon wafers. Circular pillars 3-8 µm in diameter with a pitch of 3-15 µm were defined with UV-lithography and etched to a depth of 3 µm with a DRIE process. These microstructures were combined with nanostructures fabricated by etching of black silicon.

The black silicon process was carried out in the DRIE system. No predefined mask was used; the structures were etched by perforating the native oxide layer combined with a passivation layer from the etching process. Holes in the native oxide layer were etched. With the correct choice of plasma parameters the results become cone shape structures [7]. The black silicon etch produced roughly 100 nm wide cone-like structures with an aspect ratio of about 1.

The injection molding insert (shim) was fabricated from the structured silicon wafer by deposition of a 100 nm thick layer of nickel vanadium followed by nickel electroplating. The silicon wafer was subsequently removed by a KOH etch, leaving a nickel insert with inverse polarity. A variotherm injection molding process was used to injection mold microscope slides in cyclic olefin copolymer (TOPAS 8007-04) [8]. SEM, AFM, and confocal microscopy were used to characterize the different steps in the fabrication process.

Characterization of the superhydrophobic surfaces was performed by a contact angle tennsiometer Data physics Contact Angle System OCA and a custom built tilting system with angle readout.

3 RESULTS

The fabrication process resulted in good replication in each of the fabrications steps, as shown in the SEM images in Figure

Figure 3. A small reduction in the size of microstructures occurred during the black silicon etch; the micro pillars were reduced aproxematly 0.5 µm in diameter. An AFM was used to measure the height of a single silicon pillar with black silicon and on a similar hole on the nickel shim. The resulting profile is shown in Figure 4. The height was measured to be approximately 3.2 µm and replication of black silicon in the nickel shim is clearly visible. Injection molding replicated both micro and nanostructures in the polymer (Figure 3D).

The super hydrophobic properties of the structured microscope slides were characterized by contact angle and drop roll off measurements with water. A microscope slide with water drops is shown in Figure 1. Preliminary results indicate a contact angle increase from 95° for the unstructured polymer to a maximum 150°, obtained for 3 µm pillars with a spacing of 8 µm (Figure 5). Roll of angles were measured as a function of pitch size for different pillar diameters and plotted in Figure 6.

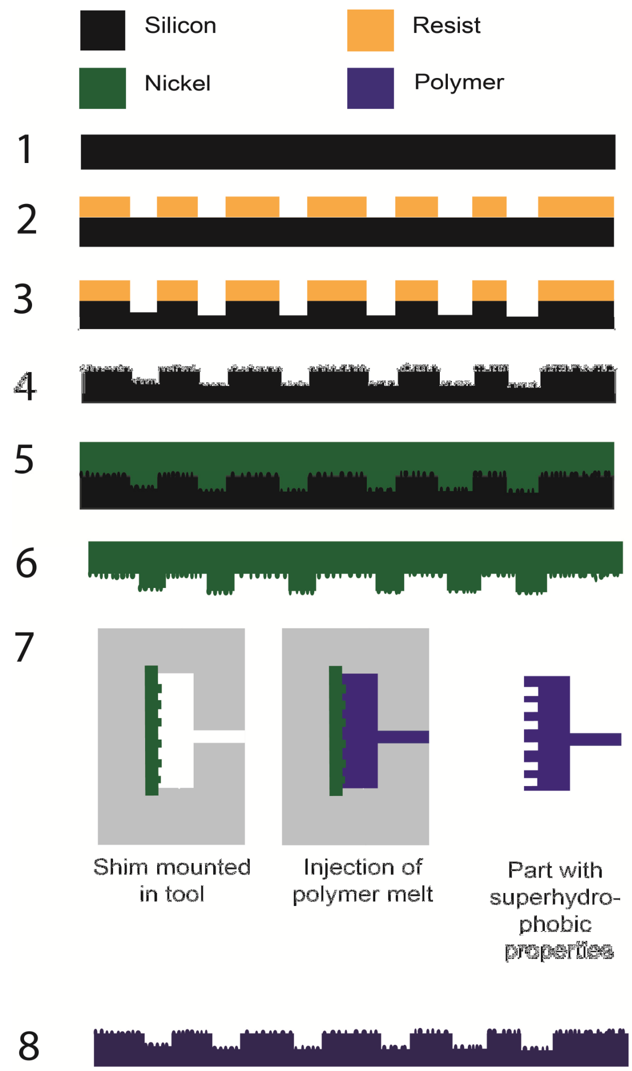

Figure 2: The entire fabrication method: 1 and 2) Lithography, 3) Dry etch , 4) resist strip and black silicon etch, 5) Electroplating of nickel shim , 6) removal of silicon wafer with KOH, 7) injection molding of polymer parts from nickel shim, 8) finished parts with super hydrophobic surfaces.

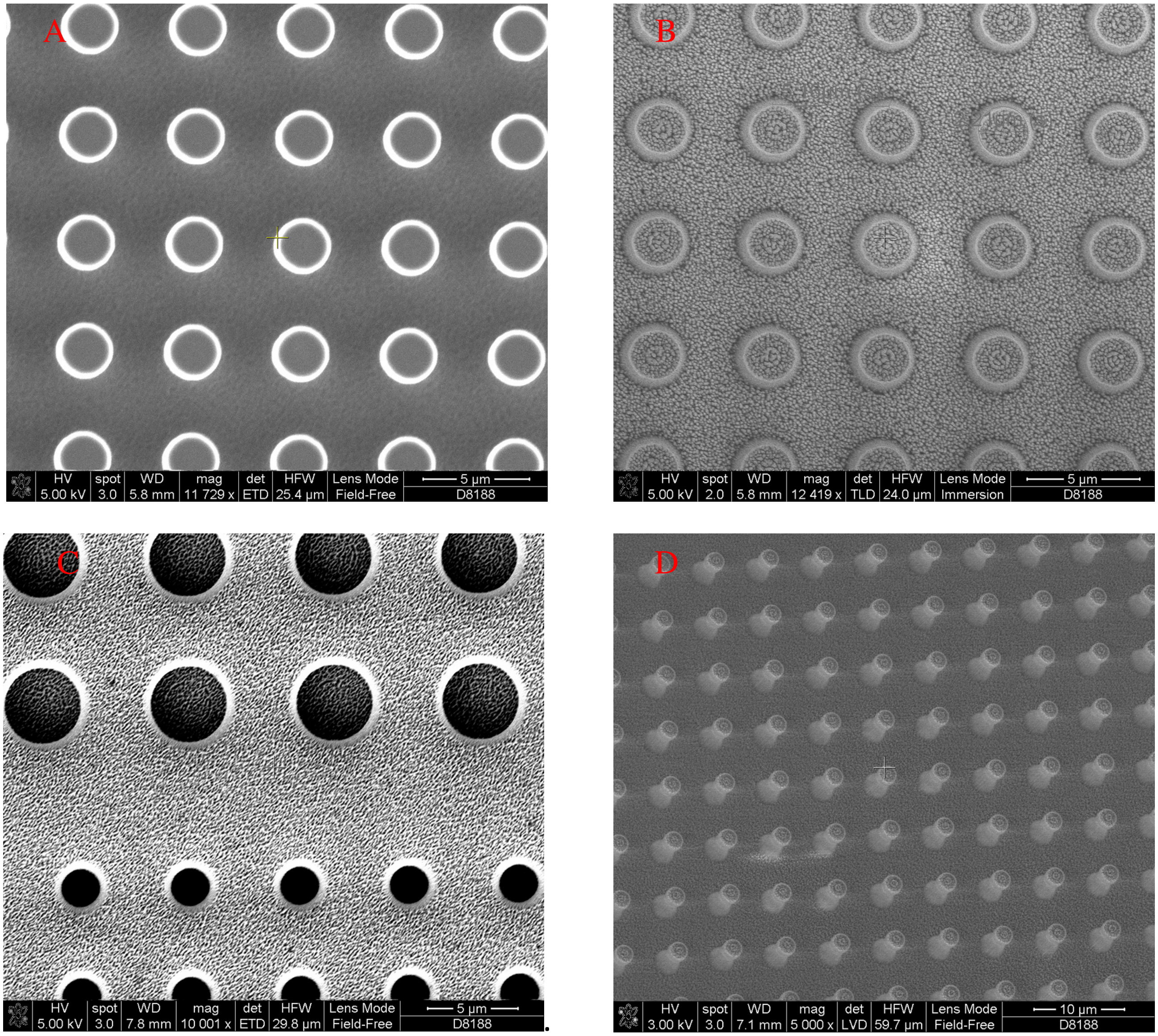

Figure 3: SEM images of different steps in the fabrication process. A) Micro pillars in etched in silicon. B) Etch of hierarchical black silicon. C) Electroplated nickel insert with inverse structures. D) Injection molded self-cleaning surface hierarchical structures.

Roll off angles decrease from approximately 45° for the areas with closely packed pillars, to below 5 degrees for areas with larger pitch size of the pillars. Similar roll off- and contact angles are reported for other super hydrophobic surfaces with hierarchical nano and microstructures [3, 4]. The lowest rolls off angles observed were in the range 1° to 5° for structures having the 8 µm spacing. It was nearly impossible to deposit a drop on the surface when the roll of angle was below 5° as it readily rolled or bounced to other test areas, or outside the structured surface. This clearly indicates that the drops do not wet the structures and are in the so-called Cassie Baxter state [9].

4 CONCLUSION

Polymer microscope slides with superimposed micro- and nanometer structures and with a minimum structure size of 100 nm were fabricated by injection molding. The microscope slides showed super hydrophobic properties; the contact angle was increased from 95° for the unstructured polymer to a maximum of 150° and the lowest drop roll of angle was approximately 1°.

5 ACKNOWLEDGEMENTS

This work is supported by the Danish Advanced Technology Foundation through the Advanced Technology Platform NanoPlast (grant no. 007-2010-2).

REFERENCES

1. Bhushan, B., Y.C. Jung, and M. Nosonovsky, *Lotus Effect: Surfaces with roughness-Induced superhydrophobicity, Self-Cleaning and low Adhesion*, in *Springer Handbook of Nanotechnology*, B. Bhushan, Editor. 2010, Springer: new york. p. 1438-1518.
2. Barthlott, W. and C. Neinhuis, *Purity of the sacred lotus, or escape from contamination in biological surfaces.* Planta, 1997. **202**(1): p. 1-8.
3. Bhushan, B., K. Koch, and Y.C. Jung, *Biomimetic hierarchical structure for self-cleaning.* Applied Physics Letters, 2008. **93**(9).
4. Puukilainen, E., et al., *Superhydrophobic polyolefin surfaces: Controlled micro- and nanostructures.* Langmuir, 2007. **23**(13): p. 7263-7268.
5. McCormick, R.M., et al., *Microchannel Electrophoretic Separations of DNA in Injection-Molded Plastic Substrates.* Analytical Chemistry, 1997. **69**(14): p. 2626-2630.
6. Sun, G., et al., *Fabrication of micro/nano dual-scale structures by improved deep reactive ion etching*. Journal of Micromechanics and Microengineering, 2010. **20**(7).
7. Kumaravelu, G., et al., *Surface texturing for silicon solar cells using reactive ion etching technique*. Conference Record of the Twenty-Ninth IEEE Photovoltaic Specialists Conference 2002. 2002. 258-261.
8. Andresen, K.O., et al., *Injection molded chips with integrated conducting polymer electrodes for electroporation of cells.* Journal of Micromechanics and Microengineering, 2010. **20**(5).
9. Cassie, A.B.D., *Contact angles.* Discussions of the Faraday Society, 1948. **3**: p. 11-16.

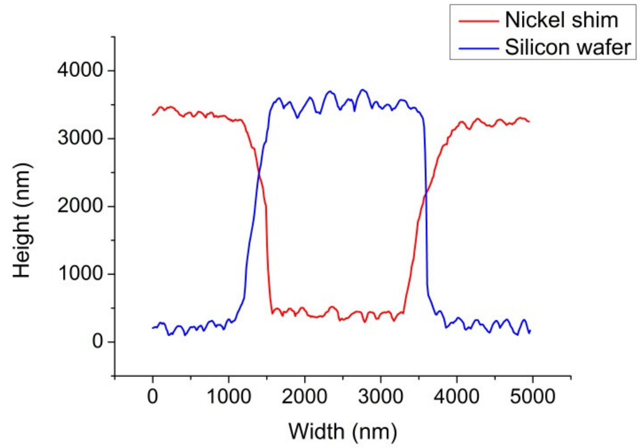

Figure 4: Profile of 2.5 µm micro pillar with hierarchical nanostructures (black silicon) and a similar hole from the electroplated nickel shim (inverse polarity).

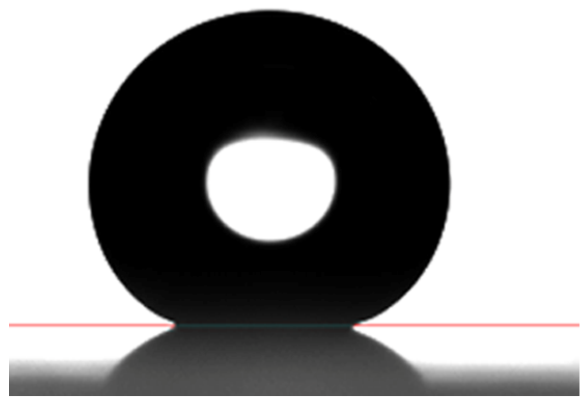

Figure 5: Drop with maximum contact angle at 150° on 3 µm pillars with a spacing of 8 µm.

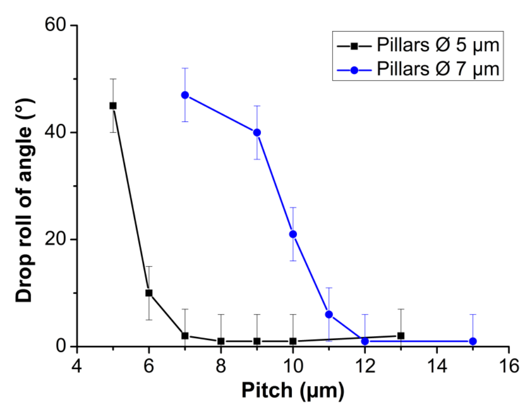

Figure 6: Drop roll of angle plotted as function of pitch.