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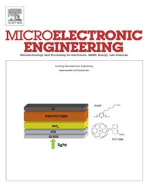

Multi-height structures in injection molded polymer

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ABSTRACT

We present the fabrication process for injection molded multi-height surface structures for studies of wetting behavior. We adapt the design of super hydrophobic structures to the fabrication constrictions imposed by industrial injection molding. This is important since many super hydrophobic surfaces are challenging to realize by injection molding due to overhanging structures and very high aspect ratios. In the fabrication process, we introduce several unconventional steps for producing the desired shapes, using a completely random mask pattern, exploiting the diffusion limited growth rates of different geometries, and electroforming a nickel mold from a polymer foil. The injection-molded samples are characterized by contact angle hysteresis obtained by the tilting method. We find that the receding contact angle depends on the surface coverage of the random surface structure, while the advancing contact angle is practically independent of the structure. Moreover, we argue that the increase in contact angle hysteresis correlates with the concentration of pinning sites among the random surface structures.

1. Introduction

Since the discovery of the special surface structures giving rise to super hydrophobic surfaces in nature researchers have sought to artificially replicate the effect by micro and nano structuring surfaces. It is widely known that the most common cause of super hydrophobicity is due to trapping of air between surface structures when liquid is applied on the surface. This composite state, the so-called Cassie–Baxter state [1], facilities low adhesion and high apparent contact angles of liquid drops on the surface. The Cassie–Baxter state is often energetically unfavorable and can collapse into the wetting state, the so called Wenzel state [2], by various transitions [3,4]. In the Wenzel state, liquid drops adhere to the surface. Keeping the droplets in the Cassie–Baxter state is therefore of key importance for maintaining super hydrophobicity [5]. Here we present a fabrication technique for realizing multi-height structures for super-hydrophobic purposes. By introducing multi-height structures, the Cassie–Baxter state cannot collapse directly into the Wenzel state but will encounter several mixed states during the transition, see Fig. 1.

For all mixed states, the adhesion between the drop and the surface is between the extreme values of the Cassie–Baxter state and the Wenzel state. This creates a gradual change in adhesion of the drop in contrast to the binary behavior seen for single height structures [5]. Overall, the multiple structure heights increases the number of states where the drop is able to roll off, thereby increasing the robustness of the super hydrophobicity. Many different approaches have been shown to achieve a super hydrophobic surface, including lithographic patterning [6], self-assembling structures [7], mask-less processes [8] and direct replication of natural water repellant surfaces [9]. In this respect, we focus on structuring the super hydrophobic surface by injection molding. Many of the artificial and natural super hydrophobic surfaces seen in literature are undesirable for injection molding since they rely on high aspect ratios or overhanging structures [10]. Therefore, we present a fabrication process comprising overlapping random patterns that gives rise to multilevel surface structures without overhang. These surface structures are designed to improve the stability of the Cassie–Baxter state, reduce the resistance for drops rolling off the surface, and are realized by industrial injection molding. For this we choose multi-height, low aspect ratio, microstructures with rounded corners. The low aspect ratio is a constraint imposed by the production method and would normally result in an unstable Cassie–Baxter state. The stability is sought improved by introducing multiple heights in the surface structures. Finally, as proposed by Krumpfer et al. [11], we developed a method to round the corners of the microstructures for reduction of roll-off resistance.

The fabrication of the final injection molded polymer sample can be broken down to a chain of steps shown in Fig. 2. The fabrication steps can also be divided into 4 different phases; fabrication of the master structures in a silicon wafer (1–4), reversing the polarity using hot embossing (5 and 6), creating mold insert by electroforming (7 and 8) and injection molding with polypropylene

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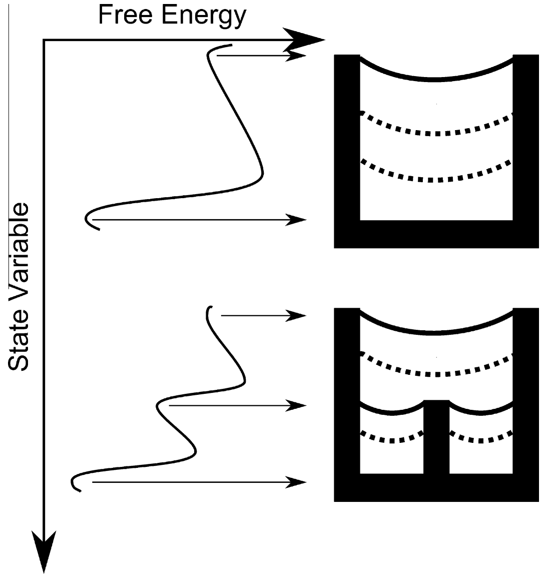

Fig. 1. Sketch illustrating the energy associated with the state of the system, solid lines being stable or meta-stable states and dashed lines being wetting transitions. By introducing a second structure height, an extra meta-stable state appears in the energy landscape.

(9 and 10). In order to get the desired rounding of protrusions we grow and remove a thermal oxide on the silicon surface. During oxidation the growth rate of the oxide is diffusion limited, resulting in different rounding at open and closed corners. This is shown in Fig. 3, where a circular pillar is oxidized and shown in profile. The corners at the tops of the pillars remain sharp while the corners at the base of the pillars are smoothened out. To utilize this effect to produce protrusions with rounded tops we define the structures as holes in the silicon master, oxidize it and reverse the polarity by imprinting in a polymer foil.

The mask used to define the surface structures consists of a matrix with 16 (4×4) fields of $6 \times 6\ \text{mm}^2$ areas where surface coverage is varied along one axis (0.22%, 0.26%, 0.30%, 0.33%) and the diameter of the dots is varied along the other (5, 7, 9 and 11 μm). To predict the specific surface coverages we simulate the structuring. The surface coverage is calculated as a function of the number of dots k by $f = 1 - (1 - \pi r^2/A)^k$, where r is dot radius, and A is area of the pattern. This equation is derived from the probability of a point in A being covered by at least one of k circles with radius r. The probabilistic nature of this equation makes it a very good approximation for a macroscopic area covered by microscopic dots. The local microscopic surface coverage might however deviate significantly from the macroscopic value.

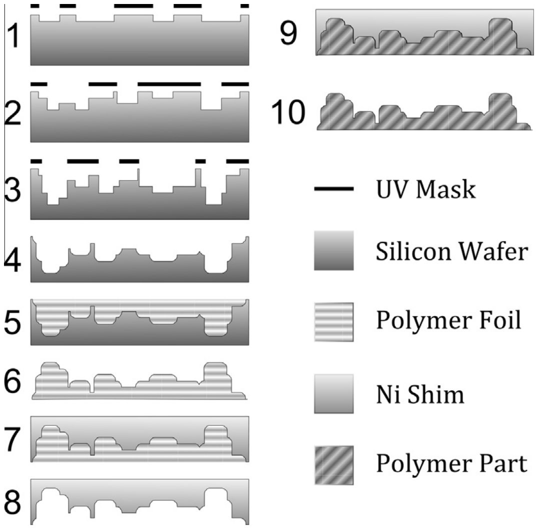

Fig. 2. Schematic drawing of the fabrication process for the multi-height structures in injection-molded polymer. (1–3) UV lithography and D-RIE etching, (4) thermal oxide growth and removal in BHF, (5 and 6) imprint in polymer foil, (7 and 8) electroforming of Ni, (9 and 10) injection molding of final part.

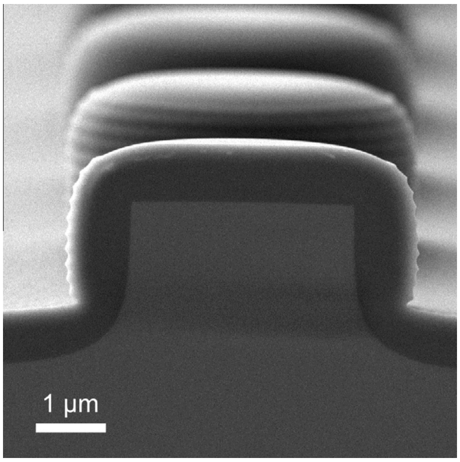

Fig. 3. SEM image of a cleaved Si pillar covered with thermally grown oxide. The morphological difference between oxide grown at open (top of pillar) and closed (base of pillar) corners is clearly visible.

2. Experimental

To fabricate the silicon master for the nickel (Ni) insert we used a single crystalline silicon (Si) wafer. Etching of microstructures was a three-step process that was repeated three consecutive times for creating the multi-height structures. First step is spin coating the silicon wafer with 4.2 μm AZ5214E photoresist and soft baking at 90 °C for 60 s (Maximus 804, ATMsse Gmbh). Second step is UV exposure by 57 mJ/cm^2 (EVG620, EVG) and development for 60 s (AZ 351B developer mixed 1:5 with water). Third step is pattern transfer by D-RIE etching (Pegasus DRIE, STS). The remainder of the photoresist was removed by Oxygen plasma (Plasma processor 300, Tepla). The random multi-height surface structure is achieved by etching to three different depths in each repetition and misaligning the mask by 0.5 mm between each exposure. Each misalignment is done perpendicular to the previous step resulting in $5 \times 5\ \text{mm}^2$ fields with the desired structure. The etched structure is shown in Fig. 4a. For the wafer presented in this paper we used etching depths of 2.8, 3.8 and 6.6 μm resulting in structure heights of 0, 2.8, 3.8, 6.6, 9.4, 10.4, and 13.2 μm depending on the combination of random overlaps of holes. By etching the smallest amount (2.8 μm) during first etching and largest amount (6.6 μm) during last etching the problems with spinning photoresist into deep trenches is minimized. If one tries to etch higher aspect ratio holes, the spinning of photoresist often fails. This can easily be seen by the naked eye and the photoresist can be removed and reapplied before etching, only resulting in a longer process time. To smoothen out structures, 1 μm of wet thermal oxide was grown and consecutively removed in BHF buffer. The silicon wafer was then coated with FDTS by molecular vapor deposition (MVD100E, Applied Microstructures Inc.). Polarity of the structures was reversed by imprinting (CNI, Nil Technology) the structures into a 300 μm thick polymer foil (TOPAS 8007s04) at 160 °C under 6 bar for 20 min. The foil was peeled off the silicon