Roll-to-Roll (R2R) Fabrication of Micro Pillar Array for Biomimetic Functionalization of Surface

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The roll-to-roll (R2R) fabrication method to make micro-scale pillar arrays for biomimetic functionalization of surfaces is presented. Inspired by the micro-structure of plants in nature, a surface with a synthetic micro-scale pillar array is fabricated via maskless photolithography. After the surface is SAM (self-assembled monolayer) coated with trichlorosilane in a vacuum desiccator, it displays a hydrophobic property even in R2R replicas of original substrate, whose properties are further characterized using various pitches and diameters. In order to perform a comparison between the original micro-pattern and its replicas, surface morphology was analyzed using scanning electron microscopy and wetting characteristics were measured via a contact angle measurement tool with a 10 μ L water droplet. Efficient roll-to-roll imprinting for a biomimetic functionalized surface has the potential for use in many fields ranging from water repelling and self-cleaning to microfluidic chips.

Keywords : Roll-to-roll process, Hydrophobic, Self-cleaning surface, Micro-pattern

1. Introduction

Some living things in nature use micro-scale structures for their existence. Scientists and engineers have made efforts to mimic such structures and have succeeded in applying the resulting structures to new types of applications. Researchers have used a biomimetic approach considering the Namib desert beetle to make self-filling devices that perform moisture harvesting; they have also used the lotus leaf to create self-cleaning devices with the concept of water repelling. The Namib desert beetle and the lotus leaf have micro-patterns on their surfaces; these patterns consist of hydrophobic or hydrophilic materials [1]. In

nature, micro-patterns on surfaces provide enhanced self-filling or self-cleaning properties depending on the surface roughness, which controls the wettability [2]. This is why micro-patterning is a significant factor in rendering a surface functional; however, there is a limitation in fabricating such microscale structures for commercial applications using the current semiconductor fabrication process. For wider adoption of biomimetic functional surfaces, it is becoming quite important to fabricate structures with more cost-effective and scalable replication technology for larger areas. In this work, in order to address such needs, we demonstrate the fabrication of a functional micro pillar array with various diameters using maskless pho-

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tolithography; we then perform replication using an R2R process for low cost fabrication.

Based on the theoretical equation of $dE=r(\gamma_{SL}-\gamma_{SA})dx+\gamma dx \cos\theta^*$, $\cos\theta^*=r\cos\theta$ that correlates surface roughness to wettability [2], we designed surface features such as pitch and diameter. In order to analyze the surface characteristics of micro-pillar arrayed surfaces, scanning electron microscopy (SEM) and contact angle measurement are used. Herein, we use a method of low cost R2R fabrication to show that such surfaces can demonstrate good performance of hydrophobic property corresponding to their material and structural combinations.

II. Experimental Section

1. Structure fabrication

Microstructures were constructed via photolithography. Before the photolithographic process, a negative photoresist (PR) of mr-DWL5 (Micro resist technology, Germany) was coated on Si substrate using a spin coater. Following the PR process, a master with a micro-scale pillar array was patterned in various diameters (1, 2, and 4 μm) via a maskless lithography system (EZ litho, Japan). The negative mold was fabricated from the master by soft lithography using PDMS (Sylgard 184, Dow Corning, Korea). Then, a stamp made out of the negative mold was applied to the surface of a quartz roller on a roll-to-roll (R2R) tool so that a desired pattern could be replicated continuously by the R2R process using a UV-curing resin (NOA 85, Norland products) on Kapton films.

2. Characterization and measurement

The original micro-pattern and R2R replicas were coated with SAM (self-assembled monolayer) of trichloro (1H,1H,2H,2H-perfluorooctyl)-silane (Sigma Aldrich) in

a vacuum desiccator for 2 hours. Surface morphology was analyzed with a scanning electron microscope (FE-SEM, JSM-7100F, JEOL, Japan) and hydrophobic wetting characteristics were measured using a contact angle measurement tool (Dataphysics, OCA15EC, Germany) with a water droplet of 10 μL .

III. Results and Discussion

In order to fabricate a bio-inspired micro-scale pillar array pattern and its replica, we used a simple two-step method: photolithography via maskless lithography and an R2R process. Both the original and the replicated surfaces demonstrated well-aligned micro-pillar array with good performance for hydrophobic wetting property. The height of the micro pillar was around 4 μm in our experiments. All samples were maintained at 1 atm 25°C and were characterized using field emission scanning electron microscopy (FE-SEM), optical microscopy (OM), and contact angle measurement.

1. Structures

Fig. 1(a) provides a schematic of the simple two-step

Figure 1. (a) Schematic images of surface fabrication method comprising photolithography, soft lithography, and R2R process. Images of (b) maskless lithography tool (EZ litho, Japan) for photolithography, and (c) R2R machine.

process using which the design of the micro-scale pillar array was fabricated via maskless lithography [Fig. 1(b)]; the array was then further replicated using the R2R process. Surfaces are additionally treated with a monolayer of trichlorosilane in order to provide a hydrophobic property. Since SAM is applied only as a monolayer, simply to enhance the wettability of the surface, the surface roughness factor can mainly be determined by the geometry of the micro-scale patterns. So, the structural integrity and the surface morphology during the replication process

are the most critical of the surface properties. In Fig. 2 we provide images of the positive and negative patterns for the $4\text{ }\mu\text{m}$ pillar array; these images indicate that the arrays are well maintained during the fabrication process.

In Figures 3 and 4, micro-scale pillar arrays patterned using photolithography and R2R replication are shown, along with the results from the contact angle measurement for various designs. In the case of the $1\text{ }\mu\text{m}$ pillar pattern, a slight bowing effect is observed due to the pattern's high aspect ratio (>4).

Figure 2. SEM images showing the fabrication results on (a) $4\text{ }\mu\text{m}$ pillar array patterned with photolithography and (b) a negative mold patterned with soft lithography.

Figure 3. SEM images of original micro-pillar array (a–c) and corresponding results from the contact angle measurements (d–f). (a, d) $1\text{ }\mu\text{m}$ pillar, $4\text{ }\mu\text{m}$ pitch, (b, e) $2\text{ }\mu\text{m}$ pillar, $4\text{ }\mu\text{m}$ pitch, (c, f) $4\text{ }\mu\text{m}$ pillar, $8\text{ }\mu\text{m}$ pitch. For (d, e, f), contact angle measurements display results of 142° , 111° , and 90° , respectively.

Figure 4. SEM images of R2R replicas from original micro-pillar array (a–c) and corresponding results from the contact angle measurements (d–f). (a, d) 1 μm pillar, 4 μm pitch, (b, e) 2 μm pillar, 4 μm pitch, (c, f) 4 μm pillar, 8 μm pitch. For (d, e, f), contact angle measurements display results of 144° , 119.5° , and 95.3° , respectively.

Likewise, in the R2R replication step, a slight modification of the surface can be observed, but both defects are not critical. Designed size, pitch, and shape are maintained.

2. Characteristics

The surface of the micro-pillar array was coated with trichlorosilane to make a hydrophobic surface. Low surface energy materials provide a chemically hydrophobic property to a coated surface, so that a water droplet can be formed on such a surface with a large contact angle (CA). The CA of each surface varies with the diameter and pitch from different patterns and also depends on whether the pattern is an original or a replica. These results are summarized in Fig. 5. In all sections, the CA of replica is generally larger than that of the original; however, the tendency of both the original and the replica is fairly similar, as can be seen in the graph, with a difference in contact angle smaller than 10° . This small difference is caused by trichlorosilane, which is de-

Figure 5. Graphs showing the measured contact angle versus the diameter (1, 2, 3 μm) and pitch (4, 4, 8 μm) of the micro-patterns, and the deviation of contact angles in the replica from those of the original. Water droplets are shown to be pinned (Wenzel state) in these experiments.

posited better on the UV-curing resin than on the photo resist. The figures indicate that the characteristics of the surfaces are maintained relatively well even after the R2R process.

Comparing samples with diameters of 1 μm and 2

μm , although their pitches are the same at $4\ \mu\text{m}$, the $1\ \mu\text{m}$ diameter sample displays a much larger CA (144° in R2R replicas) than does the $2\ \mu\text{m}$ diameter sample (119.5°). This is mainly due to the fact that the roughness factor from the $1\ \mu\text{m}$ sample is larger than that of the $2\ \mu\text{m}$ sample. In the Wenzel state, the theoretical equation of $dE=r(\gamma_{\text{SL}}-\gamma_{\text{SA}})dx+\gamma dx \cos \theta^*$ explains how surface roughness is related to wettability, where r is the roughness factor, which increases with surface roughness. Measured results correspond well to the theoretical prediction for changes in contact angle.

In the case of the sample with $4\ \mu\text{m}$ diameter and pitch of $8\ \mu\text{m}$, CA is quite different from that of the sample with $2\ \mu\text{m}$ diameter even though the roughness factors of the two samples are the same. The CA of the $2\ \mu\text{m}$ sample is 119.5° , whereas the CA of the $4\ \mu\text{m}$ sample is 95.3° . If both samples provide nano-scale surface patterns, their CA may be almost the same. But, a sample with micro-scale surface roughness is also affected by the permeation of a water droplet from its bottom to its micro-structures. As the pitch increases, the downward force increases because both the unit area and the weight increase, such that the water droplet can permeate to the bottom side of the structure. With the $4\ \mu\text{m}$ pillar array at a pitch of $8\ \mu\text{m}$, a water droplet of $10\ \mu\text{L}$ in size almost leads to the impression that the surface is flat. That is why the CA of the $4\ \mu\text{m}$ diameter sample is much smaller than that of the $2\ \mu\text{m}$ diameter sample, even though their roughness factors are the same. Microstructures should provide high enough structure to prevent this permeating effect and, apparently, the designed height of $4\ \mu\text{m}$ of the micro-pillar array used in this experiment can be seen not to have been sufficient.

IV. Conclusion

We have demonstrated functional biomimetic mi-

cro-scale pillar arrays and a potentially low cost two-step method for their fabrication. All fabricated surfaces demonstrated good performance in terms of hydrophobic property, which corresponded to their material and structural combinations. From the analyses of the surfaces, performed using SEM and contact angle measurement, we were able to observe that the designed shape and characteristics were well maintained with only a small change in contact angle of $<10^\circ$ between the original and its replica. Very little modification in structure and surface during the replication process did not critically affect functional characteristics. Contact angle generally increased as roughness factor increased. If the roughness factor is the same, the pitch determines the surface wettability. For a large enough pitch, the unit area and weight increase, causing permeation of the water droplet's bottom side into the micro-structures. We believe that an efficient fabrication of roll-to-roll imprinting for biomimetic functionalized surface has potential for use in many fields, ranging from water repelling and self-cleaning to microfluidic chips.

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