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Combination of silicon microstructures and porous cellulose nanofiber structures to improve liquid-infused-type self-cleaning function

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ABSTRACT

Various fine structures and/or low surface energy material coatings have been designed to develop self-cleaning surfaces. These structures work by trapping air in their vacant spaces. Surfaces based on liquid-infused-type design exhibit better performance than those based on the traditional design; however, their life is limited because the special liquid covering the surface drops off easily. Cellulose nanofibers (CNFs) have amphiphilic characteristics in addition to their small size; thus, an aggregated structure consisting of CNFs will have an improved liquid holding performance. This study discusses the deposition of CNF on silicon microstructured surfaces and the etching of the CNF structure to extend its self-cleaning life. The effects of microstructure design, CNF concentration, and etching conditions on the morphology and porosity of the CNF structures are comprehensively studied. Long-term performance tests were carried out to measure the sliding angle (SA) of diethylene glycol after repeated water dash operations. It was confirmed that the combined structure of highly porous CNF and silicon microstructures exhibits a durable self-cleaning function.

1. Introduction

Many functions, such as self-cleaning, catalytic activity, and anti-reflection, can be effectively enhanced by structured surfaces. A large number of fine structures and/or hydrophobic treatment procedures have been developed for self-cleaning surfaces [1–3]. Omniphobic surfaces, on which droplets of high/low surface tension liquids can slide easily, have received much attention because of their usability in a wide range of applications. A fine structure filled with a special liquid (a lubricant) in its vacant spaces is one way to achieve omniphobicity. The ability of a structure to hold the lubricant within its vacant spaces relies on the capillary forces and the chemical affinity of hydrophobic surfaces (Fig. 1a) [4]. A second route to develop omniphobic surfaces is by using the re-entrant design of fine structures [5]. Despite having many advantages, such as very low contact angle hysteresis and self-healing, liquid-infused surfaces experience problems that do not exist in the case of solid surfaces. It is easy for the lubricant to drop-off of the surfaces due to external loads or stresses, such as different liquids, high shear, and high temperature [6–8]. The loss of lubricant leads to a strong adhesion between external liquids and the surface and subsequently to a deteriorated self-cleaning performance (Fig. 1b). Therefore, an improvement in lubricant retention is critical for long-term operations. Compared to nanostructures, microstructures have greater strength but the capillary force needed to retain the lubricant is smaller [7]. Thus, a combination of a nanofiber structure and a microstructure might possibly improve the affinity of the solid structure with the lubricant (Fig. 1a), leading to a durable liquid-infused-type self-cleaning function.

The combination of a silicon micropillar array and a porous cellulose nanofiber structure deposited in the vacant spaces between the pillars is one such design. Bio-polymeric cellulose nanofibers (CNFs) with high specific surface area and amphiphilic nature can improve the affinity of the combined structure with the lubricant. Meanwhile, the silicon pillars can protect the CNF structure against external loads, such as mechanical contact. However, there are no reports available on either affinity improvement or the deposition process of such combined structures. CNF suspensions are prepared by diluting CNF hydrogels that are available after CNF manufacturing processes. Then the suspensions can be deposited easily on silicon microstructured surfaces. The problem lies with the large aggregation of CNFs after drying due to the meniscus force, strong hydrogen bonding, and mechanical entanglement between the nanofibers [9–11]. Thus, a non-uniform and low surface area CNF structure is generally obtained. Depositing a CNF suspension of appropriate concentration on a Si micropillar array with a suitable pillar pitch and rich hydroxyl surfaces can be a solution to this problem. The CNF and pillars can be linked by hydrogen bonds and mechanical entanglement, consequently limiting the aggregation. Furthermore, a uniform CNF structure can be formed between the pillars.

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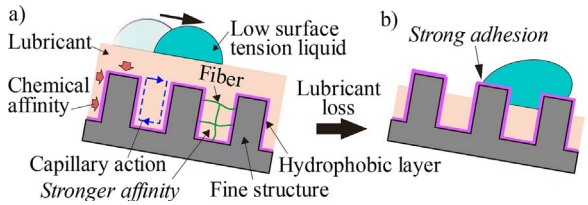

Fig. 1. A liquid-infused-type self-cleaning surface and its problems. a) The lubricant is held in the fine structure via capillary forces and chemical affinity with the hydrophobic layer. A stronger affinity with the lubricant can be obtained with an additional fiber structure [6,7]. b) A drop of a low surface tension liquid exhibits strong adhesion with the surface when the lubricant is dropped off and the structure is exposed.

The pillars can reduce aggregation but the porosity of the CNF structure is limited. To obtain a highly porous CNF structure, many efforts have been made to remove the liquid phase without the original network structure collapsing [10–14]. Surprisingly, no process for increasing the porosity of CNF structures after drying has been reported. In this investigation, we utilized an oxygen plasma etching process for increasing the porosity of dried CNF structures. Before the etching step, the CNF suspension was deposited on the silicon structure to obtain a thick CNF layer. Nevertheless CNF is susceptible to chemical action [9], all of the CNF structures can be removed by etching. Thus, a low power plasma source is preferable. The optimum etching conditions need to be investigated. Upon using oxygen plasma, large aggregated nanofibers were retained while other parts were etched. Finally, a porous CNF structure could be obtained.

This study aims to fabricate highly porous CNF-silicon surfaces via drop deposition of the CNF suspensions on silicon microstructures and subsequent oxygen plasma etching. The deposition conditions and etching conditions will be investigated in this investigation. The effects of CNF structures with and without plasma etching on the durability of the self-cleaning function will be analyzed. Finally, suitable structural designs will be discussed.

2. Experimental

2.1. Structuring and hydrophobization processes

In order to investigate the effects of CNF-silicon structures on the performance of liquid-infused surfaces, two types of combined structures were fabricated using different processes. First, silicon microstructures were fabricated via photolithography and metal-assisted chemical etching (MACE), as shown in Fig. 2. Photoresists were then spin-coated on the silicon substrates. After exposure and development, a regular pattern was produced (d is pillar diameter and p is pillar pitch,

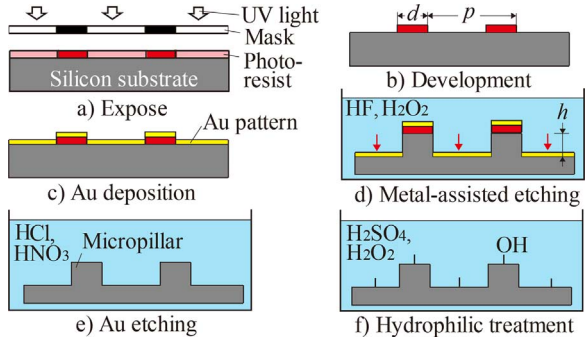

Fig. 2. Fabrication procedure of silicon microstructures. a) and b) Patterning of an OFPR photoresist on a silicon substrate by photolithography. c) An Au layer was deposited to produce an Au pattern. d) The substrate was dipped in an etchant (a solution of hydrofluoric acid and hydrogen peroxide) and an array of silicon micropillars was fabricated. e) and f) The substrate was dipped in a solution of hydrochloric acid and nitric acid for Au etching and in a solution of sulfuric acid and hydrogen peroxide for cleaning and producing a hydroxyl rich surface.

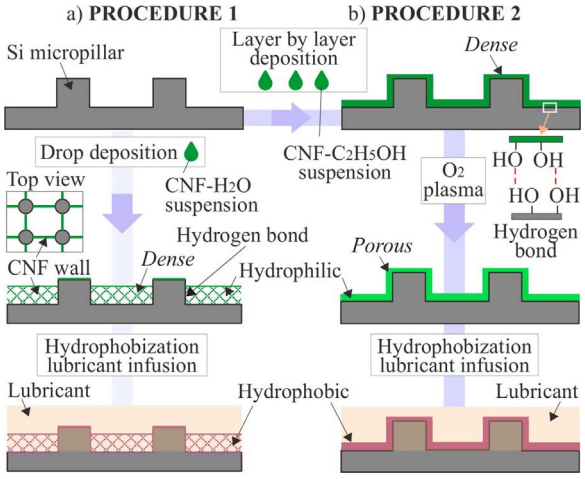

Fig. 3. Fabrication procedures of liquid-infused CNF-silicon surfaces. a) CNF suspension was deposited on silicon microstructure surfaces. With a suitable silicon micropillar pitch and appropriate CNF concentration, CNF vertical walls (parallel to the pillar direction) between the pillars were obtained. b) The CNF deposition step was repeated many times to control the thickness of the horizontal (perpendicular to the pillar direction) CNF layer. In both procedures, the CNF and silicon surfaces were linked by hydrogen bonds. The porous structure was then developed using oxygen plasma to increase the porosity of the CNF structure. The final step in both procedures is hydrophobization and lubricant infusion.

Fig. 2a and 2b). In this work, 10 μm was chosen as the diameter and the pitch was varied in the range of 20–50 μm. A layer of gold was then deposited on the substrate as a catalyst (Fig. 2c). After etching with a solution of hydrofluoric acid and hydrogen peroxide, an array of silicon micropillars was obtained (h is pillar height, Fig. 2d). The etching conditions (etchant and temperature) were chosen based on our previous studies on MACE [6,15]. CNF structures with a large surface area play a major role in lubricant retention, while silicon microstructures limit the aggregation of CNF and protect the CNF structures. Thus, a silicon structure with a high aspect ratio (ratio of pillar height and pillar diameter) is not necessary. Therefore, an etching time of 20 min was chosen. The pillar height was fixed at 15 μm (aspect ratio = 1.5) in this work. The Au layer residue was etched using a solution of nitric acid and hydrochloric acid (Fig. 2e). Before CNF deposition, the substrate was dipped in a piranha solution for cleaning and for the formation of hydroxyl groups essential for hydrogen bonding between the CNF and the silicon surface (Fig. 2f) [6]. By changing the pitch while maintaining a fixed diameter and height, CNF structures could be controlled.

Fig. 3 illustrates the two fabrication procedures used to produce either CNF vertical walls between silicon pillars (Fig. 3a: procedure 1, a simple process) or a porous CNF layer (Fig. 3b: procedure 2). In Fig. 3a, the procedure started with the drop deposition of aqueous CNF suspensions (0–0.1 wt%) prepared by diluting a commercial broad leaf CNF hydrogel (1.14 wt%). Later, the suspensions were dried at room temperature. Vertical CNF walls (parallel to the pillar direction) were formed between the pillars at the appropriate pillar pitch and suspension concentration conditions. In procedure 2, however, ethanol was used as the solvent for dilution rather than water in order to reduce the meniscus force and aggregation of CNF (subsequently reduces the drying time) [10,11]. The CNF deposition step was repeated many times (layer by layer deposition) to obtain a thick CNF layer. The profile of this layer is similar to that of the silicon microstructure. The conditions used in this step (the pitch and concentration) will be described later. They were chosen based on the results of procedure 1. In both procedures, CNFs and silicon surfaces were linked by hydrogen bonds, as shown in Fig. 3b. This layer was then etched using oxygen plasma to obtain the highly porous CNF layer. Low power oxygen plasma (Harrick plasma, RF power) usually used for cleaning or activating various substrates was used for etching. In this investigation, the values of