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Micro-and nanostructured silicon-based superomniphobic surfaces

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ABSTRACT

We report on the fabrication of silicon nanostructured superhydrophobic and superoleophobic surfaces also called "superomniphobic" surfaces. For this purpose, silicon interfaces with different surface morphologies, single or double scale structuration, were investigated. These structured surfaces were chemically treated with perfluorodecyltrichlorosilane (PFTS), a low surface energy molecule. The morphology of the resulting surfaces was characterized using scanning electron microscopy (SEM). Their wetting properties: static contact angle (CA) and contact angle hysteresis (CAH) were investigated using liquids of various surface tensions. Despite that we found that all the different morphologies display a superhydrophobic character (CA > 150° for water) and superoleophobic behavior (CA ≈ 140° for hexadecane), values of hysteresis are strongly dependent on the liquid surface tension and surface morphology. The best surface described in this study was composed of a dual scale texturation *i.e.* silicon micropillars covered by silicon nanowires. Indeed, this surface displayed high static contact angles and low hysteresis for all tested liquids.

1. Introduction

Nature offers a large variety of examples of surfaces with amazing wettability properties, like the extreme water repellency. From plant leaves to animals, this property is ascribed to the micro- and nanotexturation of the lotus leaves, the duck feather or the wings of butterflies [1]. When a rain drop is in contact, it rolls off the surface and is unable to wet it, collecting at the same time the dust particles; this behavior is called self-cleaning effect. These so-called superhydrophobic surfaces have been deeply studied and are now well known [2,3]. In order to mimic natural surfaces, roughness can be designed in a controlled fashion to significantly modify the wetting behavior. There exists a host of examples of surfaces for which a micron or sub-micron scale texturation leads to high liquid repellency [4,5].

This property can rely on the following:

- The achievement of high effective contact area between the liquid and the solid, leading to a high surface energy cost if the solid is treated with a low surface energy coating (Fig. 1A). This corresponds to a situation where the liquid is impaled by the texture. This approach has historically been proposed by Wenzel and it is denoted as Wenzel (W) state thereafter [6].
- The entrapment of air pockets between the liquid and the surface, ensuring that the liquid below the drop is mostly in contact with air (Fig. 1B). This is denoted as the Cassie–Baxter (CB) state thereafter [7]. This situation offers a very low liquid–solid friction, and this feature is particularly interesting for versatile droplet motion [8–11].

Thus to distinguish between Wenzel and Cassie–Baxter states, it is necessary to characterize the degree of impalement of the droplet sitting on or impaled inside the structuration. That is possible by measuring the difference between the advancing and receding contact angles, corresponding to the contact angle hysteresis ($\Delta\theta$), which is related to the retention force of the drop on the substrate [12].

Even though the Wenzel and Cassie–Baxter states exhibit high apparent contact angles (up to 160°), they present a totally different behavior. On most of nanotextured surfaces, in the Wenzel state, $\Delta\theta$, measured by surface tilting, is larger than 30° and the droplet remains stuck on the surface, whereas in the Cassie–Baxter state, the droplet $\Delta\theta$ can be lower than 5°. In the latter case, the liquid droplet rolls off instead of sliding once the surface is tilted by a few degrees [13]: it is called the "rolling-ball" effect [14–16].

Another point that needs to be detailed is the apparition of metastable states where liquid droplet can transit from Cassie–Baxter to Wenzel state, the more energetically stable state. While, in practice, Cassie–Baxter state is most of the time expected, one of the most widespread techniques to insure this state is to develop multi-scale structures, combining micro- and nano-metric

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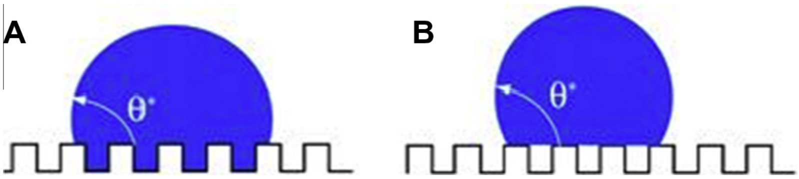

Fig. 1. A schematic illustration of the formation of composite interfaces with a droplet in the Wenzel (A) and Cassie–Baxter (B) state.

structuration. This point has been largely described and validated using different technological processes [17,18]. To extend the "rolling-ball effect" to low surface tension liquids, a structure with a re-entrant angle is required as shown by pioneering work of Tuteja et al. [19].

Theoretically, under these conditions, it is possible to obtain high contact angle even with hydrophilic surfaces. But, from an experimental view point, it is preferable to enhance the robustness of the surface (*i.e.,* preventing any transition from Cassie to Wenzel state) and then to coat the re-entrant structure with an omniphobic layer with a surface energy as low as possible. Thus, even if hydrocarbon molecules present surface energies of 35–20 mN/m, it is preferable to use fluorinated molecules that can achieve low surface energy (28–6 mN/m) [20,21]. Furthermore, Tuteja et al. recently evidenced that superoleophobicity can be achieved through an interplay with both surface geometry and chemistry. Until now, such superoleophobic surfaces were prepared by creating either a "re-entrant" curvature structure resembling micro-hoodoos, by designing a number of different nano-fiber surfaces [22,23], by an alumina nanowire forests [24] or by ZnO nanostructures [25]. Very recently, Tuteja's group has developed a stainless steel mesh uniformly coated with electrospun microbeads [26]. This surface presents a clear hierarchical structure with re-entrant features on both scales: fibers and microbeads. This surface displays amazing wetting properties: with a heptane droplet (surface tension of 20 mN/m), they measured a contact angle of 150° and a quasi-null contact angle hysteresis. In that case, the double structuration is not a key feature because similar properties were obtained using only microbeads.

Another example of hierarchical omniphobic surfaces was recently reported by Ellinas et al. [27] Such interfaces have been fabricated, *via* nanosphere lithography (polystyrene beads) on poly(methyl methacrylate) (PMMA) substrate and bearing ordered microcolumns surmounted by nanostructured polystyrene particles and coated by C_4F_8 [27]. However, these interfaces presented static CA values of 101° and 41° for hexadecane and decane, respectively and no hysteresis measurements were performed.

Zhao et al. [28] have recently described superomniphobic surfaces based on silicon micropillars. They have studied the influence of surface texturation by varying the solid area fraction (*i.e.,* by changing pillar diameter, pitch and height) and the effects of the overhang thickness and coatings on the wetting properties for water and hexadecane. Their surfaces displayed high static contact angle (SCA) and contact angle hysteresis (CAH) values of $\sim$150° and $\sim$20°, respectively, for hexadecane and SCA and CAH values of $\sim$150° and $\sim$10°, respectively for water [28,29]. All these studies evidenced that multi-scale topography is beneficial for the development of omniphobic surfaces.

The objective of this study is to develop silicon-based omniphobic surfaces and to study the role of the surface morphology on the repellency of liquids of low surface tension. For that, we report here the fabrication of omniphobic surfaces realized by different techniques achieved on silicon surfaces, leading to single or dual scale surface morphologies.

We have designed six interfaces and investigated their wetting properties. Their morphologies are described below:

- Silicon micropillars (μP-Si) obtained by standard optical lithography and dry reactive ion etching (RIE) [30].
- Silicon micropillars (μP-Si) subjected to metal-assisted electroless etching, presenting a double scale micro- and nanostructuration (μP-NanoSi).
- Silicon nanowires synthesized *via* the vapor–liquid–solid (VLS) growth mechanism [8,15,16,30,31–33]. By varying the furnace pressure and reaction time two different surface morphologies with either one or two silicon nanowires layers, SiNW-A or SiNW-B are prepared.
- These two different silicon nanowire morphologies were also grown on silicon micropillars (μP-SiNW-A and μP-SiNW-B). The resulting surfaces exhibit a double micro-nanostructuration as already described in a previous study [30].

All these interfaces were chemically modified with perfluorodecyltrichlorosilane (PFTS), a low surface energy molecule. The surface morphology was characterized using scanning electron microscopy (SEM), and the wetting properties were investigated using various molecules owing to their different surface tensions (from 72 to 21 mN/m).

2. Materials and methods

All cleaning and etching reagents were of VLSI grade. Sulfuric acid, 96% (H_2SO_4), hydrogen peroxide 30% (H_2O_2), nitric acid 69% (HNO_3), and hydrofluoric acid 48% (HF) were supplied by Amplex.

All chemicals were of reagent grade or higher and were used as received unless otherwise specified. Acetone, isopropanol, silver nitrate ($AgNO_3$) and sodium tetrafluoroborate ($NaBF_4$) were obtained from Aldrich.

2.1. Fabrication of silicon micropillars (μP-Si)

Single side polished silicon (1 0 0) oriented n-type wafers (Siltronix) (phosphorus-doped, 0.009–0.01 Ohm-cm resistivity) were used as substrates. The surface was first degreased in acetone and isopropanol, rinsed with Milli-Q water and then cleaned in a piranha solution (3:1 concentrated H_2SO_4/30% H_2O_2) for 15 min at 80 °C followed by copious rinsing with Milli-Q water. A 3.5 μm thick negative resist AZnLOF 2035 (Clariant, France) is spin-coated at 3000 rpm. A soft bake for 1 min on a hot plate at 90 °C is necessary to reduce the solvent content and to prevent resist adhesion to the exposure mask. Then, the exposure, post-exposure bake and development, are conducted for transferring the mask patterns to the resist (latent image). Then, the silicon wafer was etched using Deep Reactive Ion Etching (DRIE, Silicon Technology System) to produce high aspect ratio micropillars.

2.2. Fabrication of double scale micro- and nanosilicon interface (μP-NanoSi)

To obtain these surfaces, μ-pillars, fabricated as described above, were subjected to a metal-assisted electroless etching. Silicon nanostructures are easily prepared, in a reproducible manner,