Applied Surface Science 295 (2014) 38–43

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Fabrication of superhydrophobic and highly oleophobic silicon-based surfaces via electroless etching method

Thi Phuong Nhung Nguyen[a,b,c], Renaud Dufour[b,d], Vincent Thomy[b], Vincent Senez[b], Rabah Boukherroub[a], Yannick Coffinier[a,*]

[a] Institut de Recherche Interdisciplinaire (IRI, CNRS-USR 3078), Université Lille1, Parc de la Haute Borne, 50 Avenue de Halley, BP 70478, 59658 Villeneuve d'Ascq, France
[b] Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, CNRS-UMR 8520), Université Lille1, Cité Scientifique, Avenue Poincaré, BP 60069, 59652 Villeneuve d'Ascq, France
[c] PetroVietnam University (PVU), 6th floor, 30/4 Street, Vung Tau, Vietnam
[d] Max Planck Institute for Dynamics and Self-Organization, Am Fassberg 17, 37077 Goettingen, Germany

ARTICLE INFO

Article history:
Received 19 September 2013
Received in revised form 13 December 2013
Accepted 28 December 2013
Available online 9 January 2014

Keywords:
Silicon nanostructures
Superhydrophobic surfaces
Highly oleophobic surfaces
Non-wetting properties

ABSTRACT

This study reports on a simple method for the preparation of superhydrophobic and highly oleophobic nanostructured silicon surfaces. The technique relies on metal-assisted electroless etching of silicon in sodium tetrafluoroborate ($NaBF_4$) aqueous solution. Then, silver particles were deposited on the obtained surfaces, changing their overall physical morphology. Finally, the surfaces were coated by either C_4F_8, a fluoropolymer deposited by plasma, or by SiO_x overlayers chemically modified with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFTS) through silanization reaction. All these surfaces exhibit a superhydrophobic character (large apparent contact angle and low hysteresis with respect to water). In addition, they present high oleophobic properties, *i.e.* a high repellency to low surface energy liquids with various contact angle hysteresis, both depending on the morphology and type of coating.

1. Introduction

Surfaces displaying water apparent contact angle (ACA) greater than 150° along with low contact angle hysteresis (CAH) are typically referred to superhydrophobic surfaces. They are typically composed by a micro or nanostructuration or a combination of both covered by low surface tension compound. Such surfaces are often observed in nature on plant leaves [1,2], insect legs [3], and wings[4,5]. On these surfaces water droplets roll off easily, washing away dust-like contamination and thus conferring self-cleaning properties to the material. This remarkable property has stimulated extensive interest in the fabrication of artificial superhydrophobic surfaces as well as in understanding the underlying mechanisms of this so-called “rolling ball” effect [6–9]. However, the major limitation of superhydrophobic surfaces is that they are not able to repel low surface tension liquids such as oils and organic solvents which spread out, showing low values of apparent contact angle. Surfaces which are able to repel a wide range of liquids, including oils and organic solvents, are called superomniphobic (CA > 140°) [10]. This property is ascribed to a particular roughness topology presenting a re-entrant geometry, as it has been demonstrated using nanonails or mushrooms-like structures [10,11,12]. This extension of this repellency properties received considerable attention for potential applications in green construction, anti-fouling, self-cleaning coatings, filtration/separation, optical, and digital microfluidic systems [13–18].

The effect of surface roughness on wetting is usually explained by two well known models: The Wenzel (W) configuration assumes that the asperities between protrusions on the surface are filled by the liquid. In that case the wetting property is magnified according to Eq. (1) [19] where θ^* is the apparent contact angle on the textured surface, r the surface roughness and θ the equilibrium contact angle on the corresponding smooth surface, given by Young's relation (Eq. (2)) [20]. γ refers to the interfacial tension and subscripts s, l, and v stand for solid, liquid, and vapor phases, respectively.

$$\cos\theta^* = r \times \cos\theta \tag{1}$$

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{2}$$

The Cassie–Baxter (CB) model considers air pockets trapped below the drop, leading to a composite liquid–air and liquid–solid

* Corresponding author. Tel.: +33 3 20 19 79 87; fax: +33 3 20 19 78 84.
E-mail address: yannick.coffinier@iri.univ-lille1.fr (Y. Coffinier).

0169-4332/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.12.166

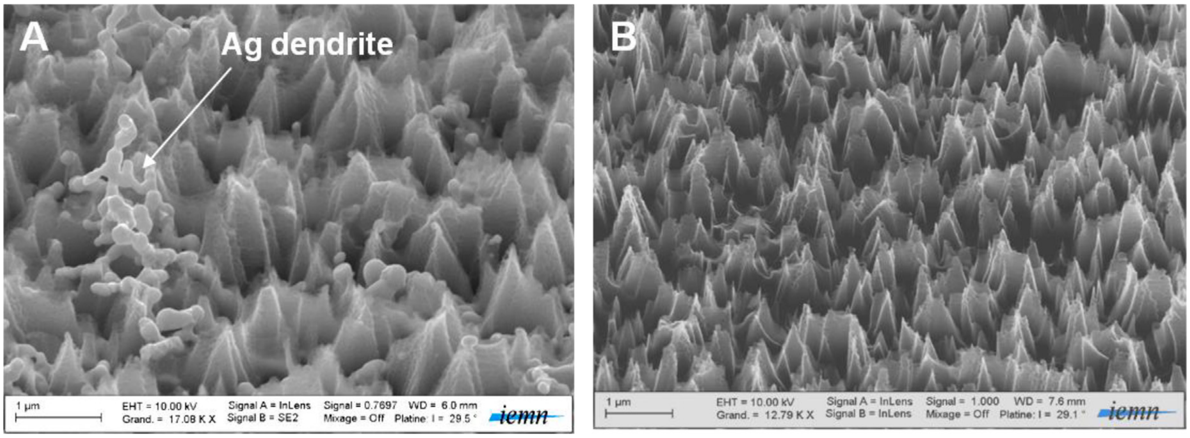

Fig. 1. SEM images of silicon nanostructures (NanoSi) prepared by chemical etching of Si (1 0 0) in $NaBF_4/AgNO_3$ (2 M/0.02 M) for 2 h at 80 °C before (A) and after silver removal (B).

interface. The droplet is thus on top of the structuration. The relation between apparent and Young angles is thus given by Eq. (3) [21] where Φ_s is the solid–liquid contacting-surface fraction.

$$\cos\theta^* = \Phi_S \times \left(1 + \cos\theta\right) - 1 \quad (3)$$

To distinguish between Wenzel and Cassie–Baxter states, it is necessary to characterize the degree of impalement of the droplet. 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 [22].

Concerning artificial superhydrophobic or oleophobic surfaces, both, surface energy and structure/roughness of the surface, must be controlled [23,24].

In this work, we report on the simple preparation of surfaces with good repellent properties towards liquids with wide range of surface tensions (from 72 to 21 mN/m). The surfaces have been developed through the optimization of roughness topology and chemistry at three levels:

1. 1st layer of texturation: Nanostructured silicon surfaces (NanoSi) prepared using an original approach based on electroless etching of crystalline silicon in $AgNO_3/NaBF_4$ aqueous solution. Recently, we have demonstrated that, by using electroless etching of silicon and notably by varying the type of etchant, its concentration, the reaction time, and the solution temperature, triangular shape nanostructures can be obtained [25].
2. 2nd layer: The nanostructured silicon surfaces were coated with Ag nanoparticles leading to modification of roughness topology and especially to the formation of re-entrant geometry enabling oleophobic behavior.
3. 3rd layer: The surfaces were coated with low surface energy compounds through silanization or C_4F_8 plasma deposition. It is known that fluoropolymer/fluorocarbon coatings display the lowest surface energies available, with Young angles on a coated flat surface around 110° for water ($\gamma_{LV} \approx 72$ mN/m) and 40–60° for oils ($\gamma_{LV} \approx 30$ mN/m) [26,27]. To ensure uniform silanization of the overall surface, an overlayer of SiO_x was deposited by PECVD on the silicon nanostructures decorated by Ag NPs. Indeed, this reaction only occurs in presence of hydroxyl groups (Si—OH) and is not expected to take place on Ag NPs.

2. Materials and methods

All cleaning (H_2O_2, 30%; H_2SO_4, 96%; HCl; HNO_3) reagents and HF were of VLSI grade and supplied by Merck. All chemicals were reagent grade or higher and were used as received unless otherwise specified. Acetone, ethanol, isopropanol, sodium tetrafluoroborate ($NaBF_4$), and silver nitrate ($AgNO_3$) were obtained from Aldrich. 1H,1H,2H,2H-perfluorodecyltrichlorosilane (PFTS) was purchased from ABCR.

2.1. Sample preparation

Single side polished (1 0 0) silicon wafers (Siltronix) (boron-doped, 0.009–0.01 Ohm cm resistivity) were used as substrates. They were first degreased in acetone and isopropanol, rinsed with Milli-Q water and 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.

2.1.1. Safety considerations

The mixture H_2SO_4/H_2O_2 (piranha) solution is a strong oxidant. It reacts violently with organic materials. It can cause severe skin burns. It must be handled with extreme care in a well-ventilated fume hood while wearing appropriate chemical safety protection.

We used HF for Ag particles deposition. HF is a hazardous acid which can result in serious tissue damage if burns were not appropriately treated. Etching of silicon should be performed in a well-ventilated fume hood with appropriate safety protections: face shield and double layered nitrile gloves.

2.2. Fabrication of silicon nanostructures (NanoSi) interfaces

In this study, we used a convenient and simple method for the fabrication of silicon nanostructured substrates from crystalline silicon *via* electroless etching method without direct manipulation of HF solution. Indeed, instead of HF, sodium tetrafluoroborate ($NaBF_4$) was used as an anisotropic etching reagent as shown by Nguyen et al. [25]. For that, Si (1 0 0) surface was dipped into an aqueous solution of $NaBF_4/AgNO_3$ (2 M/0.02 M) at 80 °C for 120 min. Then, the surface was rinsed copiously with ultrapure water and then immersed in a solution of $HNO_3/HCl/H_2O$ (1/1/1) overnight to remove all the silver particles and dendrites (deposited during silicon etching) and finally rinsed with ultrapure water and dried under a gentle flow of nitrogen. The resulting surface was called NanoSi and present a native oxide layer.