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Patterned hydrophobic–hydrophilic templates made from microwave-plasma enhanced chemical vapor deposited thin films

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Abstract

In the present research, nano-structured materials exhibiting super-hydrophobic behavior obtained by microwave-plasma enhanced chemical vapor deposition (MPECVD) had their surface chemical status altered through vacuum ultraviolet (VUV) light irradiation. Falling water droplets rolled and bounced without wetting or spreading over the initially super-hydrophobic surfaces. We demonstrate a surface preparation technique to create a patterned super-hydrophobic/super-hydrophilic substrate in which micropatterns with super-hydrophobic and super-hydrophilic regions were prepared through irradiation with VUV light. To confirm the method, growth of water droplets is observed in situ on such super-hydrophobic/super-hydrophilic micropatterns. We discuss the applicability of the super-hydrophobic/super-hydrophilic pattern to the bottom-up assembling of materials, like site-selective electroless Cu plating on patterned substrates made of paper and selective cell culture experiments.

Keywords: Micropatterns; Super-hydrophobic; Super-hydrophilic; VUV light; Microwave-plasma enhanced CVD

1. Introduction

Wettability of solid surfaces with water is well known to be governed by chemical properties and surface nanotexture. A proper nanotexture enhances the surface hydrophobic or hydrophilic properties. Also, water-contact angles on a surface are in relation to the chemical status of the respective surface. For chemically identical surfaces, water-spreading is regulated by surface morphology, i.e. by roughness. For instance, flat surfaces that have water-contact angles more than 90°, by controlling their roughness can be made to achieve super-hydrophobic status with contact angles of more than 150°. Oppositely, surfaces with water-contact angles less than 90° can be made super-hydrophilic by controlling the chemical end-groups on the surface. Therefore, patterned substrates having a surface contrast consisting of regularly arranged micro-areas with different chemical properties (obtained by changing the chemical functional groups) and/or physical properties (for instance roughness) have been frequently used as microtemplates for bottom-up fabrication of functional materials [1–11].

It is well known that for substrates consisting of silicon wafers, glass plates, polymer sheets, etc., micropatterns with hydrophobic and hydrophilic regions can be prepared by using a self-assembled monolayer (SAM) patterned by photolithography. In these cases, however, the difference in the water-contact angles, that is, one of the indices of chemical affinity, between the hydrophobic and hydrophilic regions is less than 120° even if the hydrophobic region was terminated with closely packed –CF_3 groups that show the lowest surface energy among all the solid surfaces. Besides patterning, highly hydrophobic materials with a water-contact angle of 120° or higher are extremely useful in chemistry and biological science to keep surfaces from retaining, or being fouled by, contaminants and reagents. In order to obtain a water-repellent surface showing such a great water contact angle, a proper nanotexture on its surface is crucial [12–16].

In this study, we present a general method, consisting of a two-step process combining microwave-plasma enhanced CVD (MPECVD) and VUV light irradiation, to form super-hydrophobic/super-hydrophilic regions. To validate the method,

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growth of water-droplets through condensation is monitored in situ on such a super-hydrophobic/super-hydrophilic pattern. In addition, we discuss the surface properties and their applications, especially for the bottom-up assembling of materials. Regarding the potential applications of the method we demonstrate site-selective electroless Cu plating on patterned substrates made of paper and selective cell culture experiments.

2. Experimental

A microstructure consisting of super-hydrophobic/super-hydrophilic surface regions was fabricated on substrates by using a two-step process. First, thin films of about 300 nm thickness were deposited using microwave-plasma enhanced CVD (MPECVD) in order to form a nanotextured surface. The precursor in the MPECVD was trimethylmethoxysilane, (TMMOS; $(CH_3)_3Si(OCH_3)$, Sigma Aldrich) in an Ar gas atmosphere. As a result of the thin-film deposition, the substrates became super-hydrophobic. Detailed preparation procedures have been reported previously [15]. Next, each of the super-hydrophobic samples was micropatterned, as schematically illustrated in Fig. 1. First method consisted in placing a mask in contact with the sample surface, and irradiating the sample with VUV light at a wavelength of 172 nm for 20 min at 10 Pa, as shown in Fig. 1a. The light source employed in this study was an excimer lamp (10 mW cm^{-2}, Ushio Inc., UER20-172V). Another method, illustrated in Fig. 1b, used to quickly make a pattern in a free manner, was the drawing method with an F_2 laser at 157 nm (TUI Laser ExciStar 200), with the optical path purged with Ar at atmospheric pressure.

Another method used to improve the surface repellency and to compare with the method presented previously was by employing SAMs. A SAM was prepared by CVD using octadecyltrimethoxysilane (ODS; $CH_3(CH_2)_{17}Si(OCH_3)_3$, Sigma Aldrich) as a precursor. The CVD vessel was sealed with a cap and then heated for 3 h in an oven maintained at 423 K. Details of this chemical method were described in Ref. [2].

Nanotextures of the surfaces were observed by an FE-SEM (JEOL Ltd., JSM-6330F) with an accelerating voltage of 10 keV. Water droplets formation was monitored in situ by an environmental SEM (E-SEM, Nikon ESEM-2700), equipped with a differential pumping system and a gaseous secondary electron detector [15,17–20]. The E-SEM can image a hydrated sample without drying it and even when water drops condensed on the sample surface. Water vapor was introduced into the working chamber of the E-SEM, its pressure being maintained at 800 Pa. The sample holder was cooled down to a temperature of 275.2 K, which is below the dew point at this water vapor pressure, i.e., 276.1 K. Consequently, water vapor condensed on the sample surface and formed water drops. The sample holder was tilted 60° to normal.

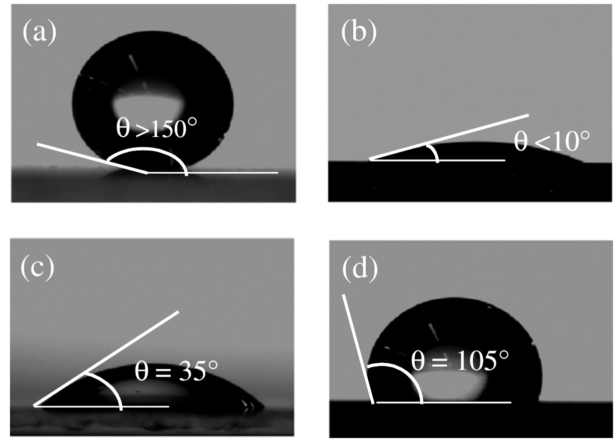

Fig. 2. Water-contact angles on different surfaces: (a) super-hydrophobic surface obtained by MPECVD, (b) super-hydrophilic surface obtained by VUV lithography, (c) clean glass surface, and (d) glass coated with a hydrophobic SAM, namely octadecyltrimethoxysilane.

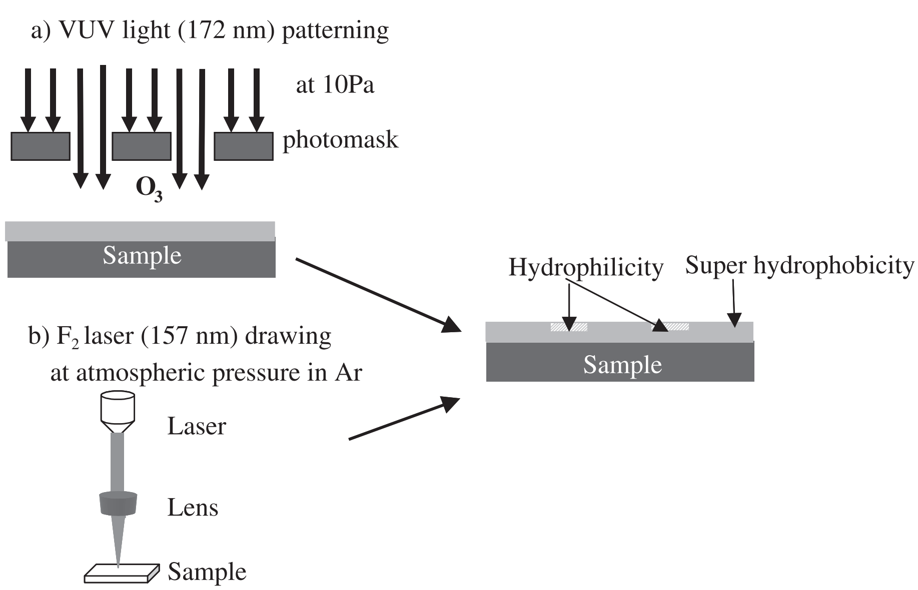

Fig. 1. Schematic illustration of the patterning process: (a) using VUV light at 172 nm from an excimer lamp and (b) using VUV light at 157 nm from an F_2 laser.