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Superhydrophobic Coatings for Microdevices

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Abstract

We have developed two simple techniques to impart superhydrophobic properties to the surfaces of microdevices. In the first approach, thin films of a fluoropolymer were spin-coated on the device surfaces followed by an oxygen plasma treatment. By varying the oxygen plasma treatment time, the water contact angles on device surface could be tuned from 120° to 169°. In the second approach, a nanoimprint process was used to create nanostructures on the devices. To fabricate nanoimprint stamps with various feature sizes, nanosphere lithography was employed to produce a monolayer of well-ordered close-packed nanoparticle array on the silicon surfaces. After oxygen plasma trimming, metal deposition and dry etching process, silicon stamps with different nanostructures were obtained. These stamps were used to imprint nanostructures on hydrophobic coatings, such as Teflon, over the device surfaces. The water contact angle as high as 167° was obtained by the second approach.

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Keywords

Superhydrophobic, nanosphere lithography, nanoimprint, coating

1. Introduction

In the development of modern technology, it is often useful to learn from nature. Many new ideas and inventions have originated from the observation of the behavior of natural materials. One recent example is the so-called “superhydrophobic” materials, which exhibit a water contact angle larger than 150°. Such superhydrophobic materials have lately attracted considerable attention because of their self-cleaning properties. In the past, it was known that a very high water contact angle could be obtained by treating the Teflon surface with oxygen plasma [1, 2]. However, it was only until the discovery of the relationship between the micro- and nano-structures of the plant surfaces and their water-repellent behavior [3, 4],

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that researchers started to realize that such superhydrophobic materials might have some important applications. For example, it has been suggested that contamination, oxidation and current conduction can be inhibited on such superhydrophobic surfaces [5], and the flow resistance in the microfluidic channels can also be reduced using the super water-repellent materials [6]. In another example, it was demonstrated that the superhydrophobic surfaces could resist the adhesion of cells and proteins [7]. The self-cleaning and anti-adhesion properties of the superhydrophobic surface could be beneficial to various applications where a clean surface is always required. However, one of the most important issues to incorporate superhydrophobic surfaces into the existing applications is that the surface modification process should be compatible with the current manufacturing techniques, especially the micro-fabrication process.

In the past few years, a variety of fabrication procedures have been proposed to prepare superhydrophobic surfaces. In general, superhydrophobic surfaces can be fabricated by coating a rough surface with low surface energy molecules, such as fluoroalkylsilanes [8] or by roughening the surface of hydrophobic materials. Many superhydrophobic surfaces have been produced by these approaches including fluoroalkylsilane modified inverse opal surfaces [9], plasma polymerization [10], anodic oxidation of aluminum [11], gel-like roughened polypropylene [12], plasma fluorination of polybutadiene [13], oxygen plasma treated poly(tetrafluoroethylene) [1, 14], densely packed aligned carbon nanotubes [15], aligned polyacrylonitrile nanofibers [16], and solidification of alkylketene dimer [17]. If superhydrophobic surfaces are to be used in a microdevice, the modification process should be compatible with the micro-fabrication techniques. For example, if one would like to engineer the surface of a microfluidic device with superhydrophobic properties to reduce the flow resistance, the superhydrophobic material should be integrated into the microfluidic system [6, 18]. Since the surfaces of the microdevices are always flat and smooth, superhydrophobic surfaces can be produced only by roughening a hydrophobic coating. However, almost none of the above-mentioned techniques can be used directly in such type of applications. Therefore, an alternative approach for producing superhydrophobic coatings on the device surface is needed.

Here we describe two simple fabrication processes to modify the surface of the device to achieve a very high water contact angle. In the first approach, the device was first coated with a thin film of hydrophobic materials, fluoropolymer in this case, and then oxygen plasma was used to create superhydrophobic surfaces. However, only in some cases, the chemical properties of the hydrophobic materials could be altered by the oxygen plasma treatment [19]. Therefore, a second technique has been developed where the nanostructures can be created on the device surfaces by a nanoimprint process [20]. Both of these approaches are compatible with the micro-fabrication process.

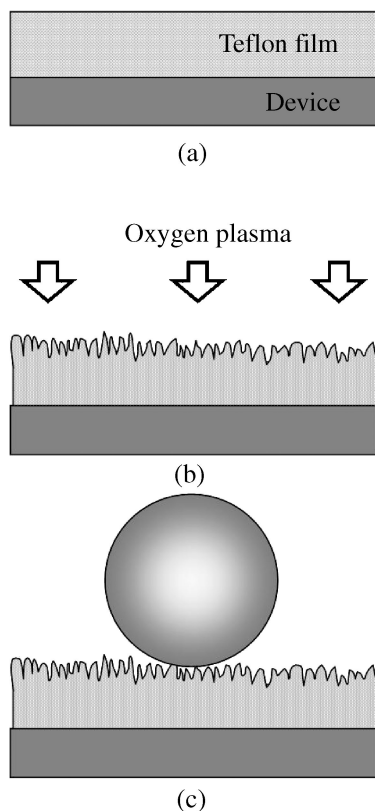


Figure 1. Schematic for producing a superhydrophobic coating on device surfaces using oxygen plasma treatment. (a) The surface of the device is coated with a layer of fluoropolymer (Teflon). (b) Oxygen plasma treatment is used to roughen the surface of fluoropolymer. (c) A superhydrophobic surface is obtained after the oxygen plasma treatment.

2. Experimental Section

2.1. Oxygen Plasma Treatment

One simple approach to create a superhydrophobic surface on a device is to coat the device with a layer of hydrophobic material followed by an oxygen plasma treatment, which roughens the surface of the coating material. The schematic for such process is depicted in Fig. 1. Since ITO glasses are widely used as the substrates in many industrial applications, such as liquid crystal displays, touch panels, solar cells and microfluidic systems, ITO glasses have been used to mimic the device surface in these experiments [21–23]. In the first step of this process, a thin layer of fluoropolymer poly [tetrafluoroethylene-co-2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole] (Teflon AF, DuPont) was spin coated on the ITO glass at 1000 rpm for 1 min. The thickness of the fluoropolymer was measured to be about 5 μm . The fluoropolymer covered ITO glass was then baked on a hot plate at 150°C for 30 min. After baking, the water contact angle was measured to be 120°. The

water contact angle was measured by the sessile drop method where the image of a sessile drop on the sample surface was recorded from its edge through an optical microscope and the contact angle was evaluated from the image by a Dataphysics-SCA20 program. The superhydrophobic surface could be produced by using an oxygen plasma treatment (Oxford Plasmalab 80 Plus, 80 W) with O₂ gas (20 sccm) at a total pressure of 25 mTorr.

2.2. Nanoimprint Process

An alternative approach to fabricate a superhydrophobic surface on a device is to utilize the nanoimprint technique to create nanostructures on the chip surfaces, which are coated with a thin film of hydrophobic materials. The fabrication scheme for a superhydrophobic surface using nanoimprint is illustrated in Fig. 2. To conduct nanoimprint lithography, the first step is to fabricate the stamp for nanoimprint. Previously [24–26], we demonstrated a simple technique to fabricate nanoimprint stamp by nanosphere lithography. In this process, a monodispersed polystyrene dispersion with 400 nm diameter beads (Bangs Laboratories, Inc., Fishers, IN) was

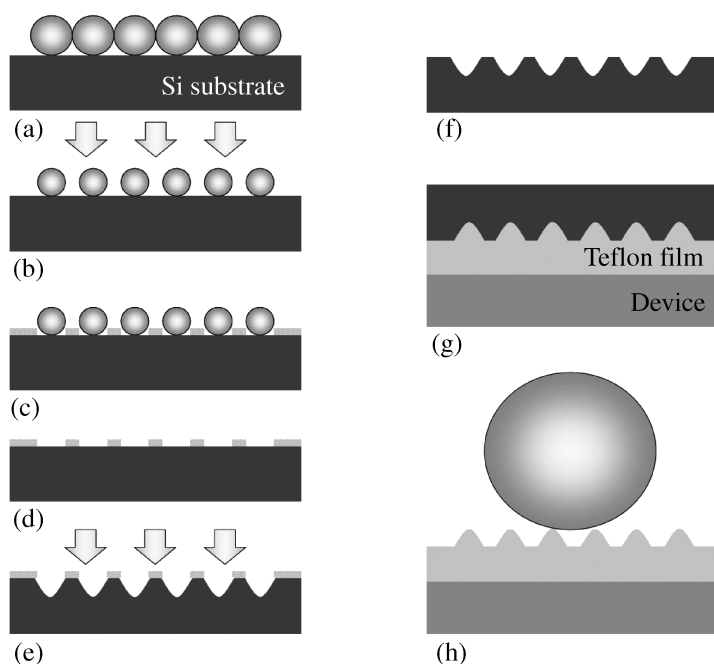


Figure 2. Schematic for creating a superhydrophobic coating on device surfaces using nanoimprint process. (a) The silicon substrate is coated with a single layer of well-ordered polystyrene beads. (b) Oxygen plasma is used to reduce the size of polystyrene beads. (c) A layer of chromium is coated on top of the polystyrene beads. (d) Polystyrene beads are then removed by CH₂Cl₂ solution. (e) The silicon wafer is etched by RIE. (f) The nanoimprint stamp is obtained by removing the chromium layer using CR-7 etchant. (g) The stamp is pressed against the device coated with fluoropolymer. (h) After removing the stamp from the device surface, nanostructure on the surface is obtained.

used to produce self-assembled close packed two-dimensional colloidal crystals on a silicon wafer. These two-dimensional colloidal crystals were then used as the template to produce stamps for nanoimprint. To vary the surface fraction of the nanoimprint stamp, the size of the polystyrene beads was trimmed by oxygen plasma etching (Oxford Plasmalab 80 Plus, 50 W, 20 sccm O₂), which reduced the diameter of the polystyrene beads while keeping their separation distance unchanged. The diameter of the polystyrene beads could be changed from 400 nm to 200 nm. To fabricate nanoimprint stamp, a 50 nm thick chromium layer was deposited on top of the trimmed polystyrene beads. Then the polystyrene beads were dissolved in dichloromethane. A dry etching process was used to etch the silicon wafer in an RIE etcher (Oxford Plasmalab 80 Plus, 110 W, 45 sccm SF₆, 5 sccm O₂). After the dry etching process and removing chromium layer by CR-7 etchant, the silicon stamp (30 × 30 mm²) with periodic nanopores was obtained.

To create a superhydrophobic surface on the ITO glass by the nanoimprint process, a 1 μm thick layer of polymer (Teflon AF) was coated on the ITO glass. Then the nanoimprint stamp was pressed against the polymer coated ITO glass under 70 mbar pressure at 150°C for 30 min. After removing the stamp, nanostructures with desired dimension can be fabricated on the device surfaces.

3. Result and Discussion

3.1. Oxygen Plasma Treatment

It has been demonstrated that the oxygen plasma can be used to roughen the surface of Teflon to produce superhydrophobic surfaces [1]. The same concept has been modified in this experiment by using the fluoropolymer coating (Teflon AF), which can be easily applied to device surfaces. Shown in Fig. 3 are the SEM images of the fluoropolymer before and after 12 min of oxygen plasma treatment. As a result of oxygen plasma roughening, nanostructures with diameters in the range of 100 nm can be seen from the SEM images. Depending on the time of oxygen plasma treatment, the surface roughness increased from 0.5 nm to 35 nm, whereas

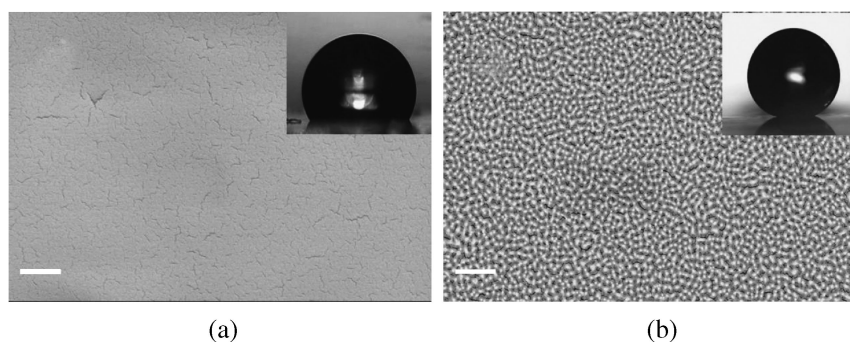


Figure 3. SEM images of (a) flat (b) roughened fluoropolymer surfaces. Inset: water droplets on both surfaces.

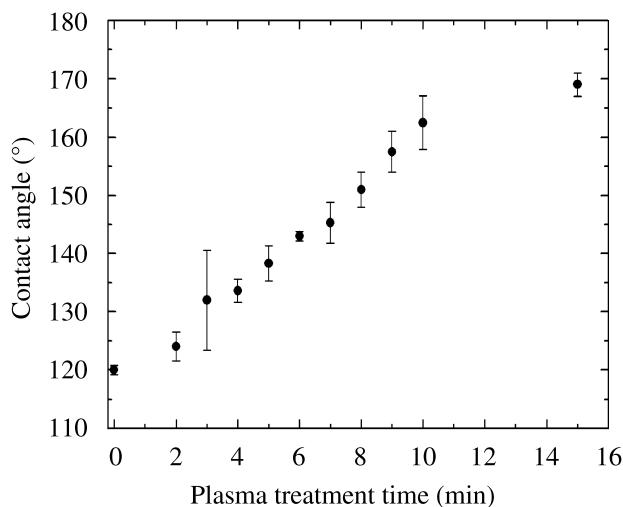


Figure 4. Water contact angle measured on the roughened fluoropolymer surface as a function of oxygen plasma treatment time.

the water contact angle on the roughened fluoropolymer surface varied from 120° to 167° as depicted in Fig. 4. In a word, the hydrophobicity of the surface can be tailored by controlling the oxygen plasma treatment time.

In some applications, it may be desirable to use thin film coatings other than fluoropolymer. However, the oxygen plasma treatment may change the surface chemistry of the coating materials. In the case of Teflon AF, the major effect of oxygen treatment is etching. No significant changes in peak shape and position were observed in the XPS spectra of the fluoropolymer before and after oxygen plasma treatment. And the percentages of the XPS peak areas changed only slightly from 77% (F), 13% (C), 10% (O) for the flat fluoropolymer to 75.6% (F), 12.7% (C), 11.7% (O) for the roughened fluoropolymer. However, if other types of coatings are used, such as SU8 photoresist, poly(dimethylsiloxane) (PDMS) or polyethylene, additional oxygen peaks in the XPS spectra were observed indicating that the surfaces had been chemically modified. In fact, the surfaces of the SU-8 photoresist and PDMS changed from hydrophobic to hydrophilic after the oxygen plasma treatment [19]. Therefore, the oxygen plasma roughening process may not be extended to other types of coatings.

3.2. Nanoimprint Process

In a previous experiment, we had utilized nanosphere lithography to create well-ordered nanostructures with tunable hydrophobicity on the surface [27]. However, such process is not compatible with micro-fabrication process. We have modified this technique by transferring the pattern of nanostructure into the silicon stamp and the nanostructures can be replicated by nanoimprint process. In other experiments, we had demonstrated that it was possible to create nanoimprint stamp with different

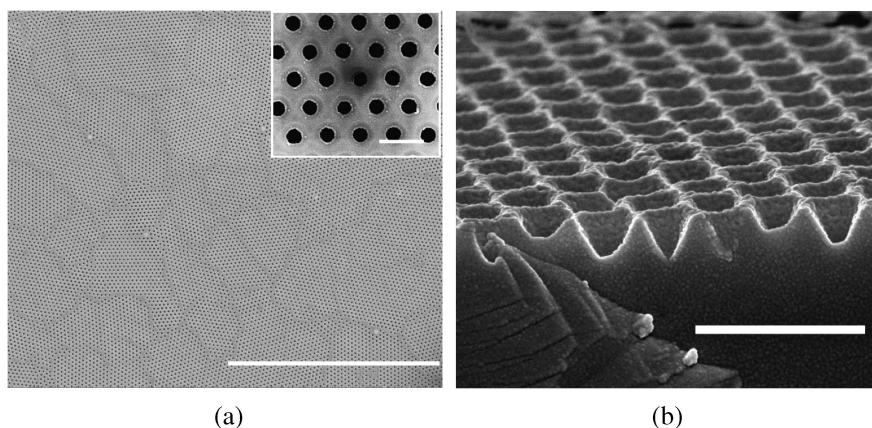


Figure 5. SEM images of the nanoimprint stamp created by nanosphere lithography. (a) Bar: 2 μm ; inset bar: 500 nm; (b) bar: 1 μm , the angle of SEM view: 60°.

dimensions of nanostructures by a combination of nanosphere lithography and oxygen plasma etching [25, 26]. The silicon nanopillar arrays with different shapes and diameters have been obtained by this approach. Following the fabrication process described in the Experimental Section, arrays of nanopores with 200 nm diameter and 300 nm in depth were created as shown in Fig. 5. To prepare a superhydrophobic coating on the device, the device was first coated with a layer of hydrophobic polymer (Teflon AF in this case). Then the stamp was pressed against the device for 30 min. After removing the stamp, a layer of nanostructure on the surface was obtained. Figure 6 shows SEM image of the imprinted nanostructures on the ITO glass surface. A water contact angle up to 168° was obtained by this approach.

Both approaches described here can be used to create superhydrophobic coatings on the device. The advantage of the oxygen plasma is the ease in the fabrication process. However, the oxygen plasma treatment often introduces chemical modification on the surface. For example, the PDMS surface could be changed to hydrophilic after oxygen plasma etching due to the formation of OH^- groups on the surface. On the other hand, there is no chemical modification on the surface in the nanoimprint process. Therefore, the nanoimprint process can be extended to all types of hydrophobic coatings.

4. Conclusion

In summary, we have developed two techniques to impart superhydrophobic property to the surfaces of devices. In the first approach, oxygen plasma treatment was used to roughen the Teflon coating whose surface water contact angle could be tuned from 120° to 168° by varying the oxygen plasma treatment time. However, the application of the oxygen plasma process is limited to fluoropolymers. In the second approach, nanoimprint process was used to create nanostructures on the

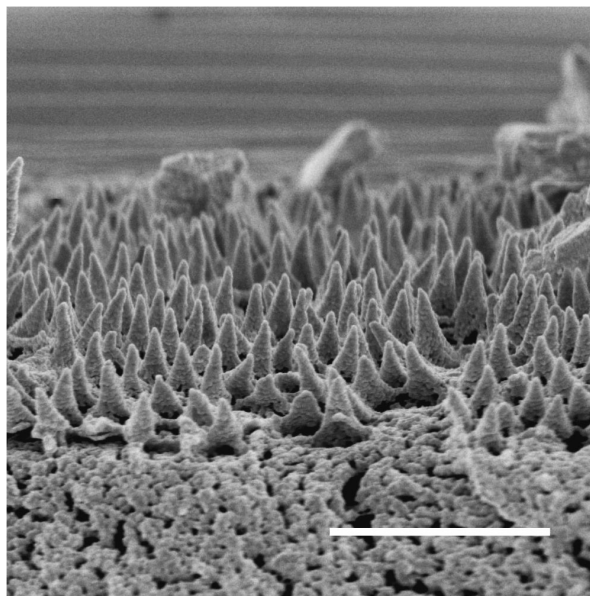


Figure 6. SEM image of the imprinted nanostructure on the ITO glass surface. Bar: 1.5 μm , the angle of SEM view: 60°.

device surfaces where the water contact angle as high as 167° was obtained. In principle, the nanoimprint process can be applied to all types of hydrophobic coatings.

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