

Synthesis of hydrophilic to superhydrophobic SU8 surfaces

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ABSTRACT: In published literature, it is widely reported that the plasma treatment and functionalization with Octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM) can individually alter the wetting properties of SU8 surface. A combination of the two approaches gives better results and the synergism of the two approaches produces a superhydrophobic SU8 surface, which is presented in this work. We have investigated various composition of plasma for treatment of SU8 surfaces and permuted the treated SU8 surfaces with deposition of OTS SAM. In all such synergized experiments, we obtained water contact angle higher than 150°, which is much higher than the one that can be obtained with individual application of the two approaches. The combined approach presented in this work is suitable for bulk production of superhydrophobic surface, and is a mask-less process, which makes it cost effective. The surface topography, wetting, and chemical properties of SU8 surfaces were characterized using the contact angle goniometry, atomic force microscopy, FTIR, Raman, and XPS spectra. The superhydrophobic SU8 surfaces were observed to be stable even after five months. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, 132, 41934.

KEYWORDS: functionalization of polymers; microfluidics; surfaces and interfaces

Received 14 August 2014; accepted 28 December 2014

DOI: 10.1002/app.41934

INTRODUCTION

Numerous studies have been performed to achieve the superhydrophobic surfaces by altering the wetting property of solid surfaces. It is well known that the wetting behavior of a solid surface is governed by surface structure and chemical composition on the surface. The wetting behavior of a liquid drop on the surface was originally defined by Wenzel and Cassie-Baxter states.^{1–3} A wide variety of materials have been studied to create superhydrophobic surfaces. Because of ease of fabrication silicon and polymers materials like poly-dimethyl-siloxane (PDMS), polymethyl-methacrylate (PMMA), and SU8 are most widely used materials to create a superhydrophobic surface.^{4–11} SU8 is the material of choice for Bio-MEMS and microfluidics devices and allows for simple processing, less fabrication time, and optical transparency.^{12–15} SU8 is a negative photo resists and exhibits hydrophobic behavior with water contact angle (WCA) of ~90°. SU8 photo resist consists of EPONTM resin which contains a cyclopentanone, polycarbonate, and photo acid generator.^{16–18} The making of SU8 hydrophilic surfaces using oxygen plasma is widely reported in Refs. 19–23. The effect of other plasma such as fluorine (SF₆, CF₄) combined with oxygen plasma had been also investigated for alteration of hydrophobicity of SU8.^{24–28}

In this article, we are reporting superhydrophobic SU8 surface achieved by combining the synergistic effect of

Octadecyltrichlorosilane (OTS, Cl₃Si (CH₃)₁₇) self assembled monolayer (SAM) on micro/nano textured surface of SU8. The scheme of the process is described in Figure 1. After the absorption of alkylsilane SAMs, the terminal methyl groups (—CH₃) reacts with a textured surface to introduce the desired functionality. The micro/nano texturing on SU8 surface had been produced by plasma treatment. OTS, self assembled monolayer deposition is one of the most extensively known and widely used ways to influence the chemical and physical properties of various surfaces.^{29–31} We have shown that the superhydrophobicity with WCA larger than 150° and hydrophilicity with WCA less than 90° both can be achieved by plasma treated SU8 with and without chemical deposition of organosilane monolayer. Moreover, we obtained superhydrophobic SU8 surface using a mask free methods.

EXPERIMENTAL

Substrate Preparation

Single side polished p-type silicon wafers (100) were used as substrate. SU8 (Microchem, SU8-2002) negative photo resist were used for experiments. The silicon wafers were cleaned in H₂SO₄ (98%) and H₂O₂ (30%) mixture of 3:1 ratio for 15 min to remove organic contaminations. The samples were rinsed thoroughly with DI water followed by drying with nitrogen gas. After cleaning, the SU8 photoresist was spin coated at 500 rpm

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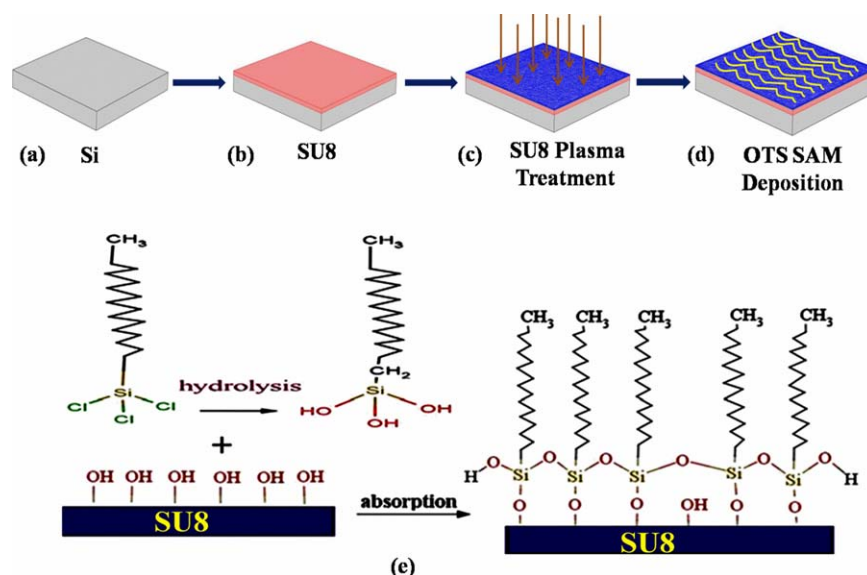


Figure 1. Schematic process flow for OTS SAM deposition on plasma treated surface: (a) Cleaned Si wafer, (b) SU8 Spinning, (c) Plasma treatment, (d) OTS SAM depositions, and (e) Formation mechanism of OTS SAM on SU8 surface. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for 5 s followed by 3000 rpm for 30 s. The coated substrate was then soft baked on a hotplate at 70°C for 2 min and then ramped up to 90°C for 2 min. The substrate was then allowed to cool down at room temperature (25°C). After baking, the SU8 coated silicon substrate was flood exposed to UV light for 10 s. Immediately after UV exposure, the SU8 substrate was post baked at 70°C for 2 min and ramped up to 90°C for 5 min. Finally, exposed substrate was developed in SU8 developer (Microchem developer) for 25 s to make sure that the exposed SU8 cross linked appropriately. The SU8 coated substrate was then cut in to small pieces of sizes $1 \times 1 \text{ cm}^2$ for further experiments. Three set of samples were used for experimental work, first set of samples were prepared by treatment with oxygen plasma, next set of samples were prepared by SF_6 plasma treatment and third set was obtained by combination of SF_6 and O_2 plasma treatment of SU8 surface.

Plasma Treatments

Plasma treatments of the prepared sample were done using the reactive ion etching (RIE) plasma source. The plasma treatment of samples surface was carried out to achieve a minimum effect on topography of SU8 surface and was done without SU8 patterning. Three different plasma environments were used for changing the surface properties of SU8 surface namely (a) SF_6 , (b) O_2 , (c) and a combination of SF_6 and O_2 . We employed plasma treatment of SU8 surfaces at power of 50 W, with chamber pressure 100 mTorr. All three set of samples were used for plasma treatment. Each plasma treated sample has been assigned a sample ID as S_i (for SF_6), O_i (for O_2), and SO_i (for $\text{SF}_6 + \text{O}_2$) plasma, where $i = 10, 30, 60 \text{ s}$.

Formation of OTS SAM

Untreated and two set of plasma treated SU8 surface were used for deposition of OTS SAM. To form high quality SAM it is very important to ensure a high level of cleanliness to minimize contamination. Among many materials available for SAM, OTS

is the most common organosilane used in the formation of SAM, mainly because of the fact that in OTS deposition process is easy, it is readily available, and it forms good, dense layers. The SU8 plasma treated sample were dipped into a toluene/OTS solution to allow the OTS to uniformly self assemble on the sample surfaces, and held in the glove box for 2 h to facilitate the SAM. The samples were rinsed sequentially with toluene, dried by argon flow. All chemicals used to form self assembled monolayer were purchased from Sigma Aldrich and were used directly without any treatment. We choose toluene (anhydrous, 99.8%, Aldrich) as the solvent for all of the solutions.

Characterization

The surface roughness measurements of untreated, plasma treated, and OTS SAM modified surfaces were conducted with atomic force microscope (AFM) BRUKER in tapping mode to obtain the information on topography of the plasma treated SU8 surfaces. The apparent water contact angle on treated surfaces were measured using contact angle goniometer (Data Physics) under ambient temperature ($25 \pm 1^\circ\text{C}$) and relative humidity (48–50%) using droplet of 5 μL deionized water. The WCA of each sample was measured five times across the sample surface using sessile drop method by dispensing 5 μL drop of DI water on the sample surface. The surface chemistry before and after OTS SAM deposition were characterized using the Raman spectroscopy (Lab Ram), FTIR (Thermo-Nicolet 6700), and X-ray Photoelectron spectroscopy (Axis Ultra).

RESULTS AND DISCUSSION

The effect of plasma treatment on wetting properties was studied by comparing the WCA of the treated surface with untreated surface and treated surface before and after OTS SAM deposition. The surface topography of plasma treated surface with corresponding surface roughness values is shown in Figure 2. The change in roughness after OTS deposition on plasma treated

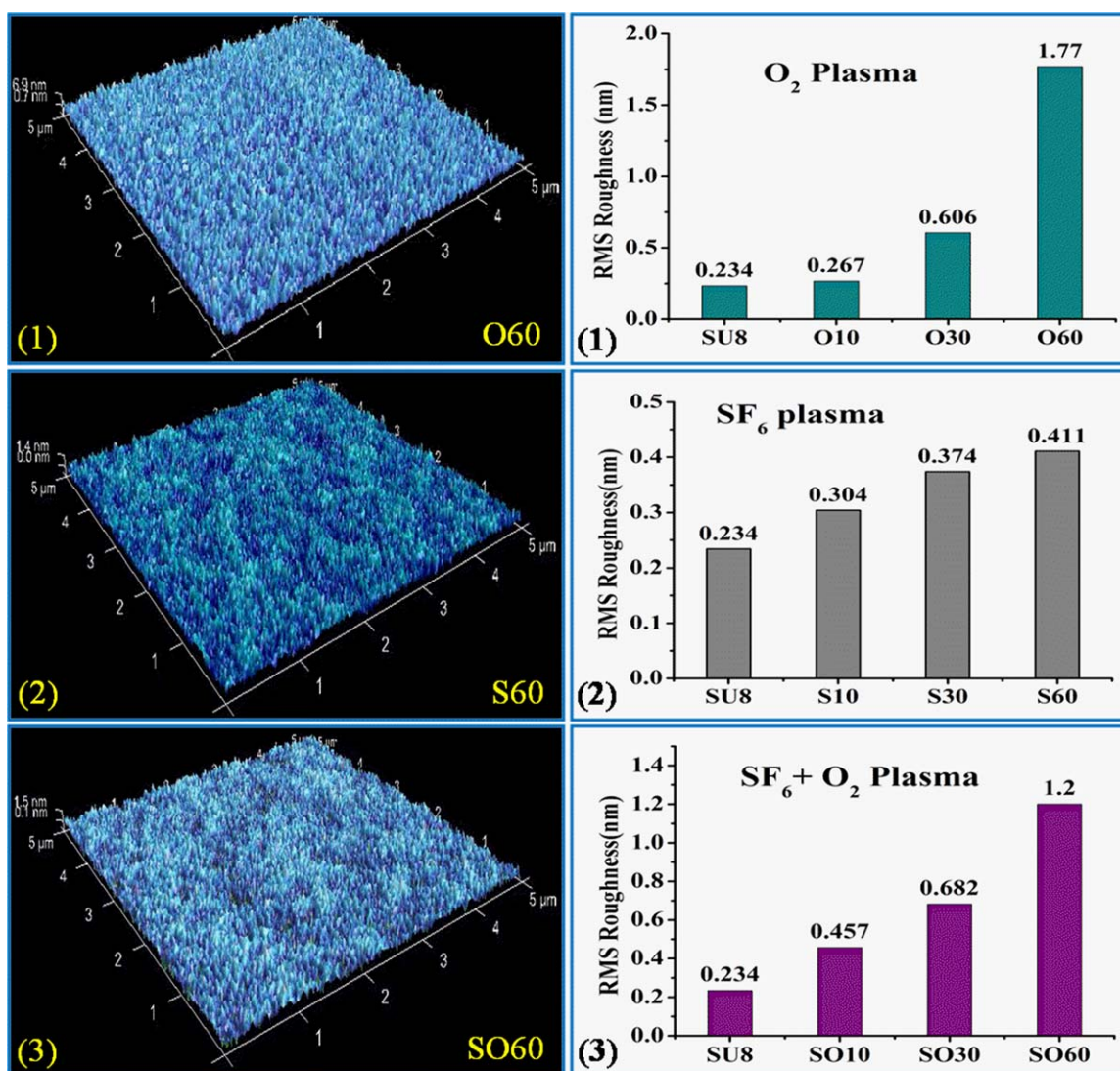


Figure 2. (a) Surface topography of plasma treated SU8 without OTS SAM Modification: (1) O60, (2) S60, (3) SO60; (b) RMS Roughness of bare SU8 and plasma treated SU8: (1) for O₂ plasma, (2) for SF₆ plasma, and (3) for SF₆ + O₂ plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

surface was also obtained with AFM as shown in Figure 4. The change in wetting behavior was observed immediately after the plasma treatment too. The measured WCA values before and after plasma treatment are shown in Figure 3(a). The WCA significantly increases after functionalization with OTS SAM on plasma treated surface as illustrated in Figure 3(b). The contact angle hysteresis also measured is shown in Figure 5. The plasma treatment affected the surface chemistry, which was analyzed using the FTIR spectra. The FTIR spectra of all samples under this study are shown in Figure 6 and were confirmed with Raman spectra shown in Figure 7. The XPS of the samples surfaces was also analyzed for untreated and treated OTS SAM SU8 surface are shown in Figure 8. We also characterized surface modifications with SAM for all plasma treatment and bare SU8 after three and five months and found that not much alteration of the surface wetting behavior occurred as can be seen from results shown in Figure 9.

Wetting Behavior of Plasma Treated SU8 Surface

The plasma treatment of SU8 was carried out using fluorine (SF₆) and oxygen (O₂) based plasma chemistries. The parameters for plasma treatment were chosen so as to cause minimum effect on the surface topography. The untreated SU8 surface exhibits a very smooth surface with an rms roughness value 0.234 ± 0.02 nm [Figure 2(b)]. The corresponding surface topography of untreated SU8 is presented in Supporting Information [Figure S1(b)] with schematic diagram of process flow of plasma treatment [Figure S1(c)]. The effects of plasma treatment increased the surface rms roughness and completely changed wettability of SU8 surfaces. In published literature, SU8 is reported as hydrophobic with WCA $\approx 90^\circ \pm 2^\circ$ ²⁰ and also is hydrophilic with WCA $< 90^\circ$.²⁶ From the plasma treatment experiment SU8 does exhibits hydrophobic property with WCA $\approx 90^\circ \pm 2^\circ$ [Figure 3(a) and Supporting Information Figure S1(a)]. The effect of oxygen plasma treatment and mixture

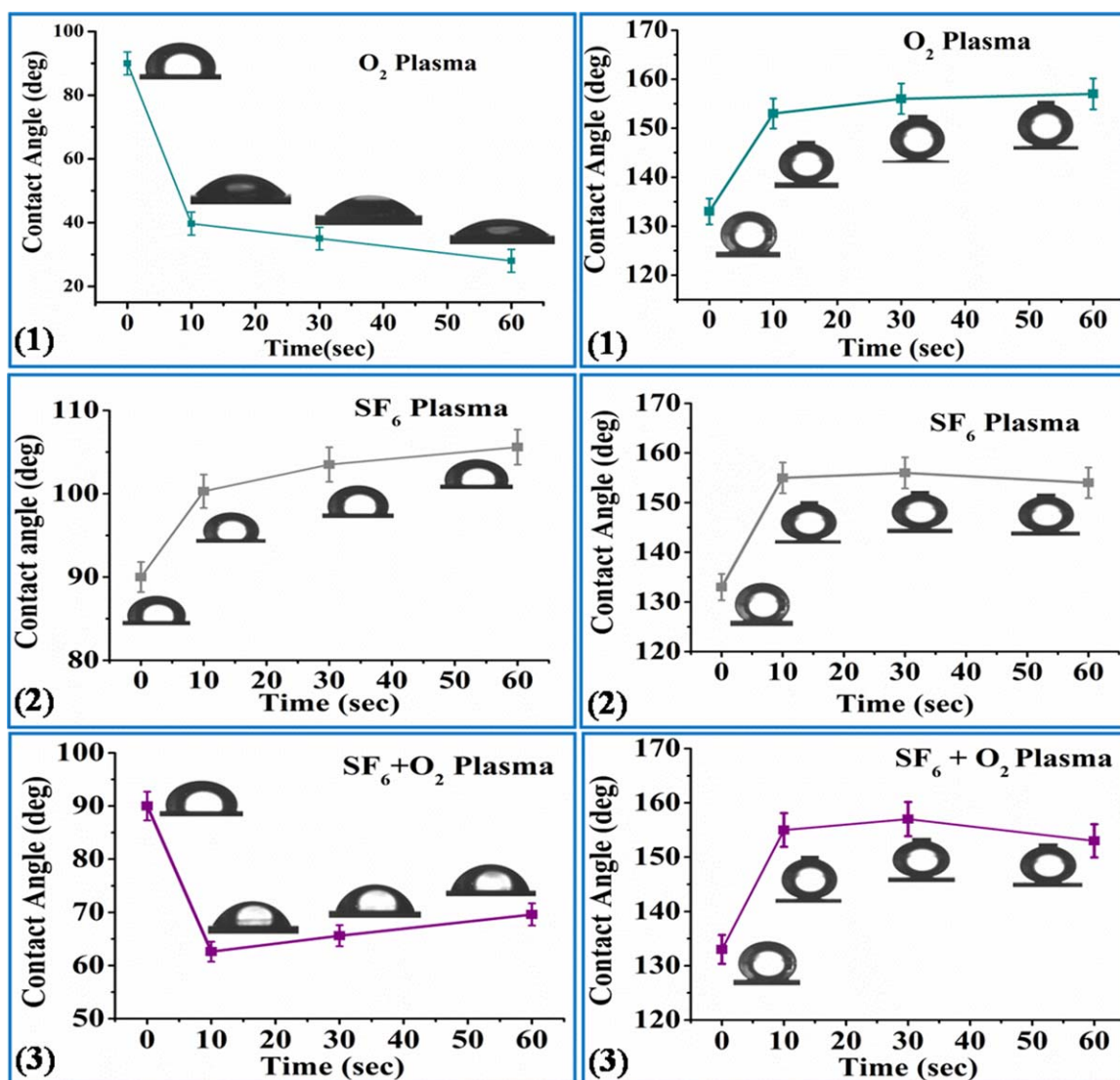


Figure 3. (a) WCA of plasma treated SU8 surface without OTS modification. (b) WCA of plasma treated SU8 surface with OTS modification (1) for O₂ plasma, (2) for SF₆ plasma, and (3) for SF₆+O₂ plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of SF₆ + O₂ plasma significantly enhanced the wetting of SU8 surface and became more hydrophilic, whereas SF₆ treatment improves the hydrophobicity of the surface as illustrated in Figure 3(a2).

Oxygen (O₂) Plasma Treatment. The oxygen plasma treatment has prominent effect on the surface topography. Oxygen plasma is widely used to enhance the hydrophilic behavior of SU8.¹⁹ In the present work, the parameters for the oxygen plasma treatment were chosen to achieve wetting and increased surface roughness for improving the hydrophilicity of SU8. It was observed that, with treatment time 10–60 s the roughness of SU8 surface increased and corresponding surface topography is illustrated in Figure 2(a1) and Supporting Information Figure S2(a). The rms roughness of the surface changed to 0.444, 0.606, and 1.77 nm depending on the plasma duration as shown in Figure 2(b1). The treatment with oxygen led to roughing the surface and induced very high wettability. The SU8 surface becomes more hydrophilic after oxygen treatment and WCA

reduced from 90° for untreated SU8 to $39.7^\circ \pm 2^\circ$, $35^\circ \pm 2^\circ$, and $28^\circ \pm 2^\circ$ with respect to different plasma treatment duration [Figures 3 (a1) and Supporting Information Figure S3(a)].

Fluorine (SF₆) Plasma Treatment. The fluorine (SF₆) based plasma is widely used and studied for treatment of SU8 surface.²⁴ The fluorine plasma treatment was optimized by controlling the parameter of RIE etching by number of experiments. The nature of dependency on SF₆ treatment time in reducing the surface roughness is illustrated in Figure 2(a2). The SF₆ treatment for 60 s makes surface more rough as compared to other treatment time. The corresponding surface topography for S60 is shown in Figure 2(a2). The surface topography for SF₆ plasma treated SU8 for sample S10 and S30 shown in Supporting Information Figure S2(b) with S60 sample. The observed rms roughness changed from 0.234 nm (SU8) to 0.304 nm, 0.374 nm, and 0.411 nm with time duration of 10, 30, and 60 s, respectively [Figure 2(b2)]. The plasma effect change the surface wetting behavior with

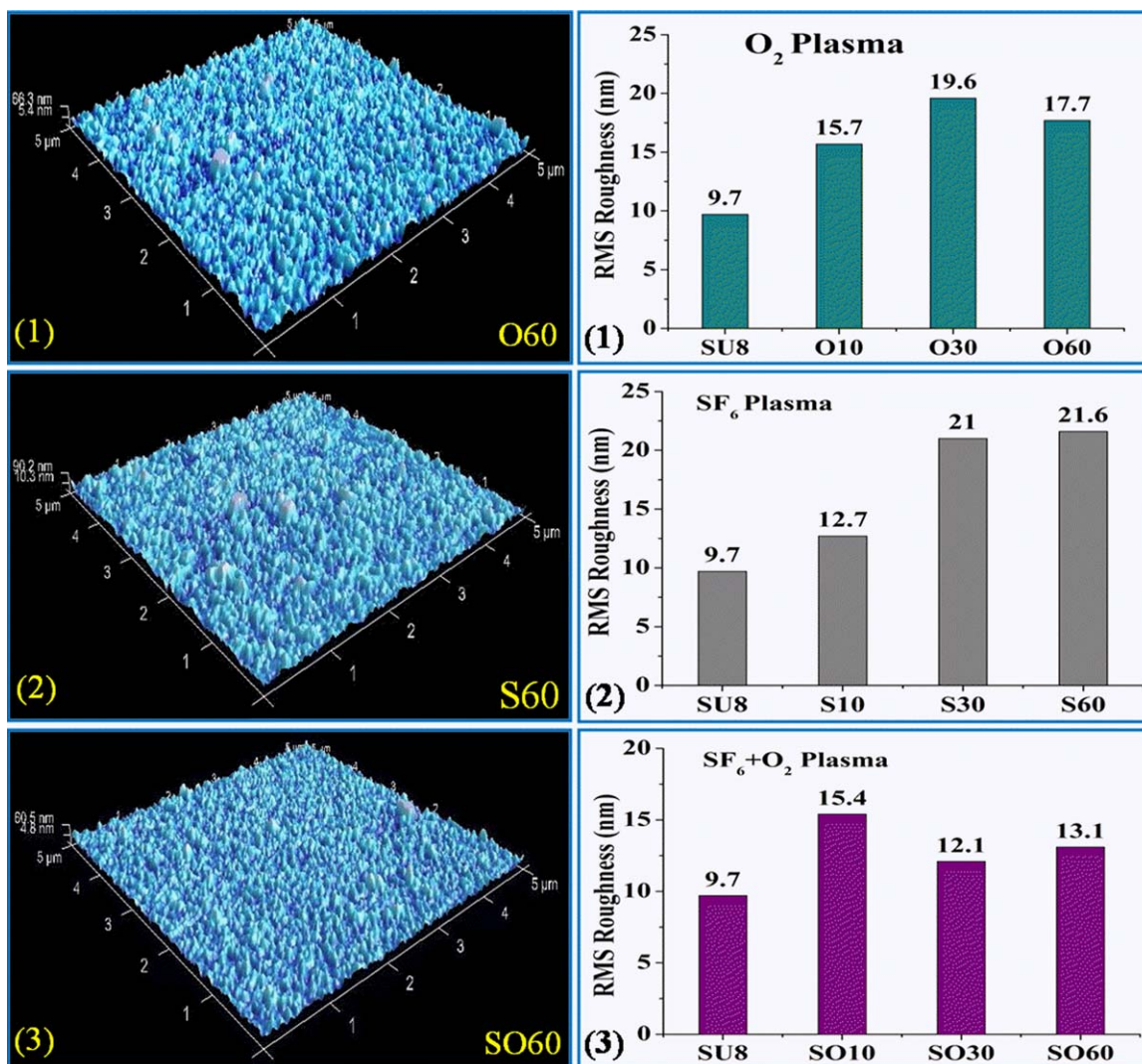


Figure 4. (a) Surface topography of OTS Modified plasma treated SU8: (1) O60, (2) SO60, (3) S60. (b) RMS roughness of OTS modified untreated and plasma treated SU8: (1) for O₂ plasma, (2) for SF₆ + O₂ plasma, and (3) for SF₆ plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

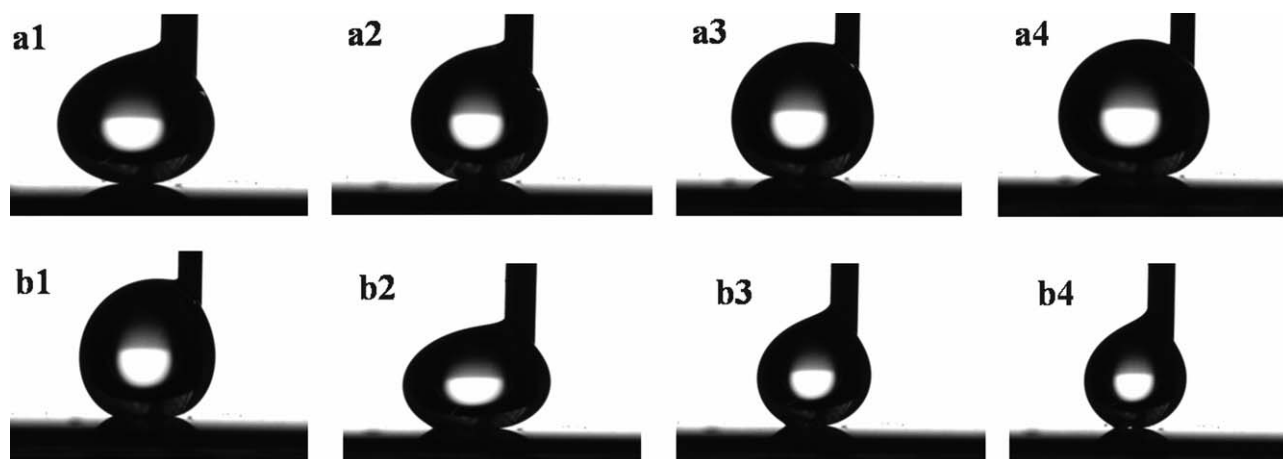


Figure 5. Contact angle hysteresis measurements (a) Advancing angle and (b) Receding angle.

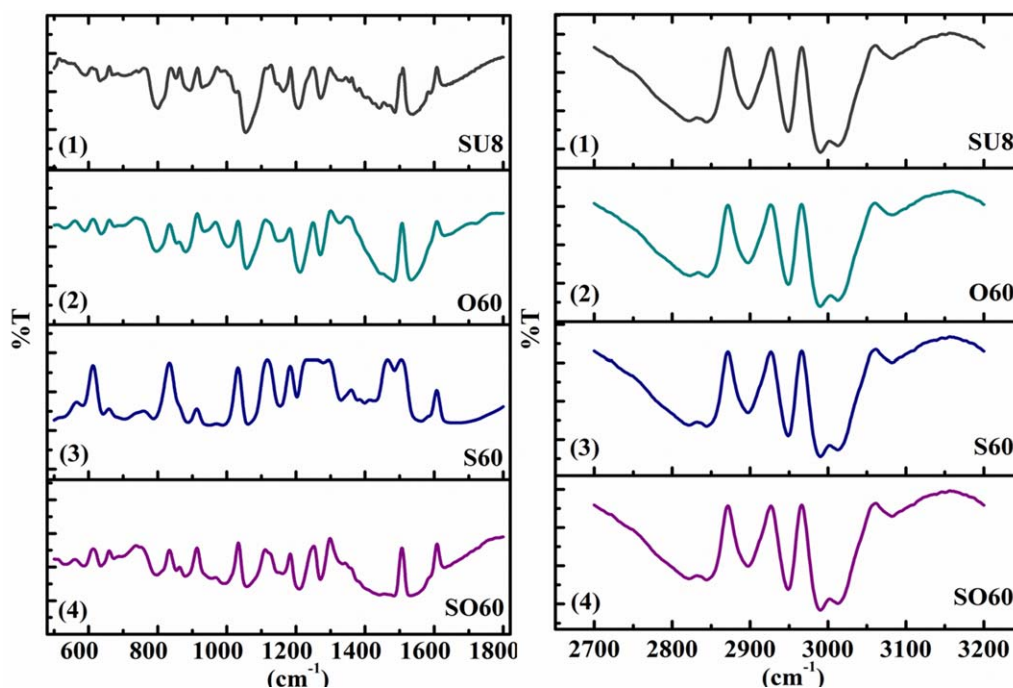


Figure 6. (a) FTIR spectra of plasma treated without OTS SU8 surface, (b) FTIR Spectra of plasma treated with OTS SU8 surface (1) bare SU8, (2) O60, (3) S60, and (4) SO60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

variation of time duration. It was found that the SF_6 plasma treatment improved the wettability behavior and provides the hydrophobic surface with WCA of $100.3^\circ \pm 2^\circ$, $103.5^\circ \pm 2^\circ$, and $105.6^\circ \pm 2^\circ$ [Figure 3(a2) and Supporting Information Figure S3(b)] as compared to untreated SU8 (WCA $\approx 90^\circ \pm 2^\circ$). There was not considerable change observed in WCA after 60 s plasma treatment.

Fluorine (SF_6) and Oxygen (O_2) Plasma Treatment. Additions of O_2 in SF_6 plasma affect the roughness change response of SU8 because of dilution of the fluorine plasma. The treatment with mixture of fluorine (SF_6) and oxygen (O_2) plasma caused rougher surface as compared to that obtained with O_2 and also untreated SU8 surface. The corresponding surface topography for SO60 is shown in Figure 2(a3). The surface topography for

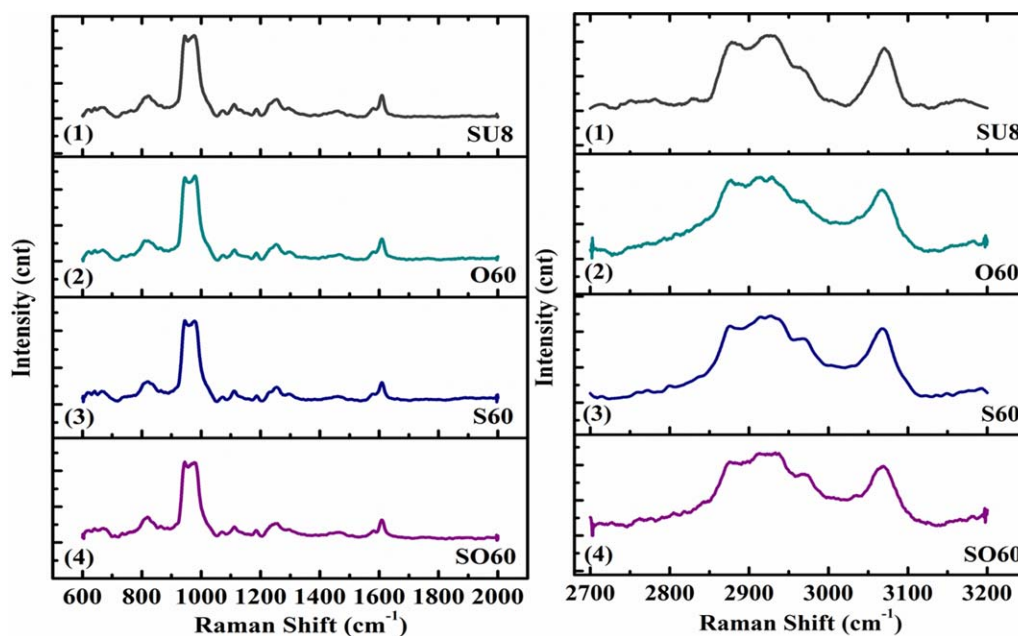


Figure 7. (a) Raman spectra of plasma treated without OTS SU8 surface. (b) Raman spectra of plasma treated with OTS SU8 surface (1) bare SU8, (2) O60, (3) SO60, and (4) S60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

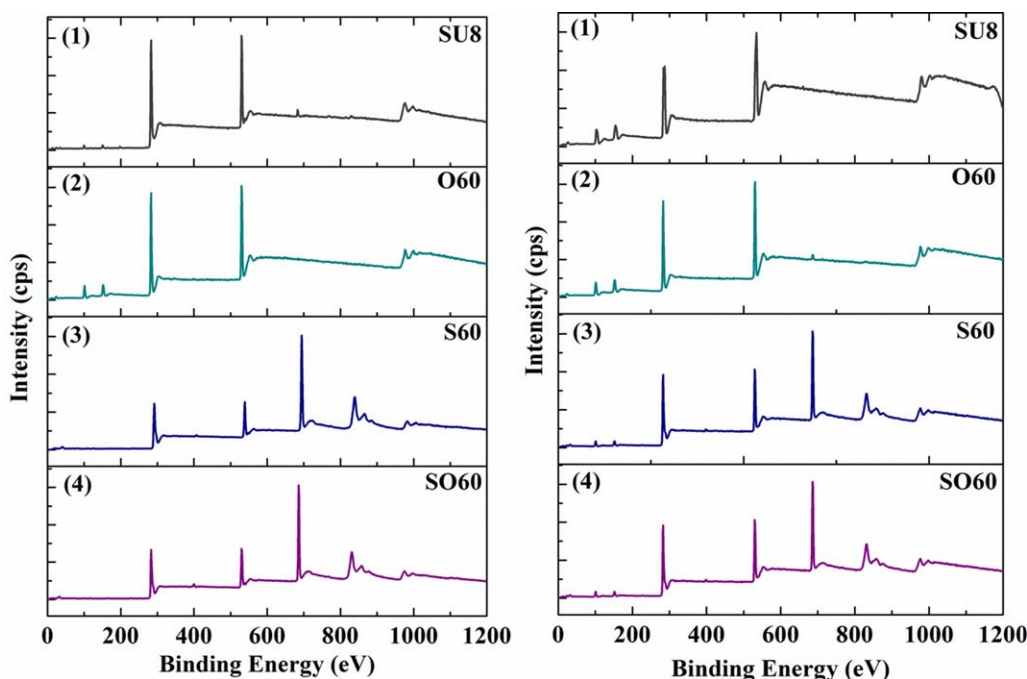


Figure 8. (a) XPS spectra of plasma treated without OTS SU8 surface. (b) XPS spectra of plasma treated with OTS SU8 surface (1) bare SU8, (2) O60, (3) SO60, and (4) S60. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

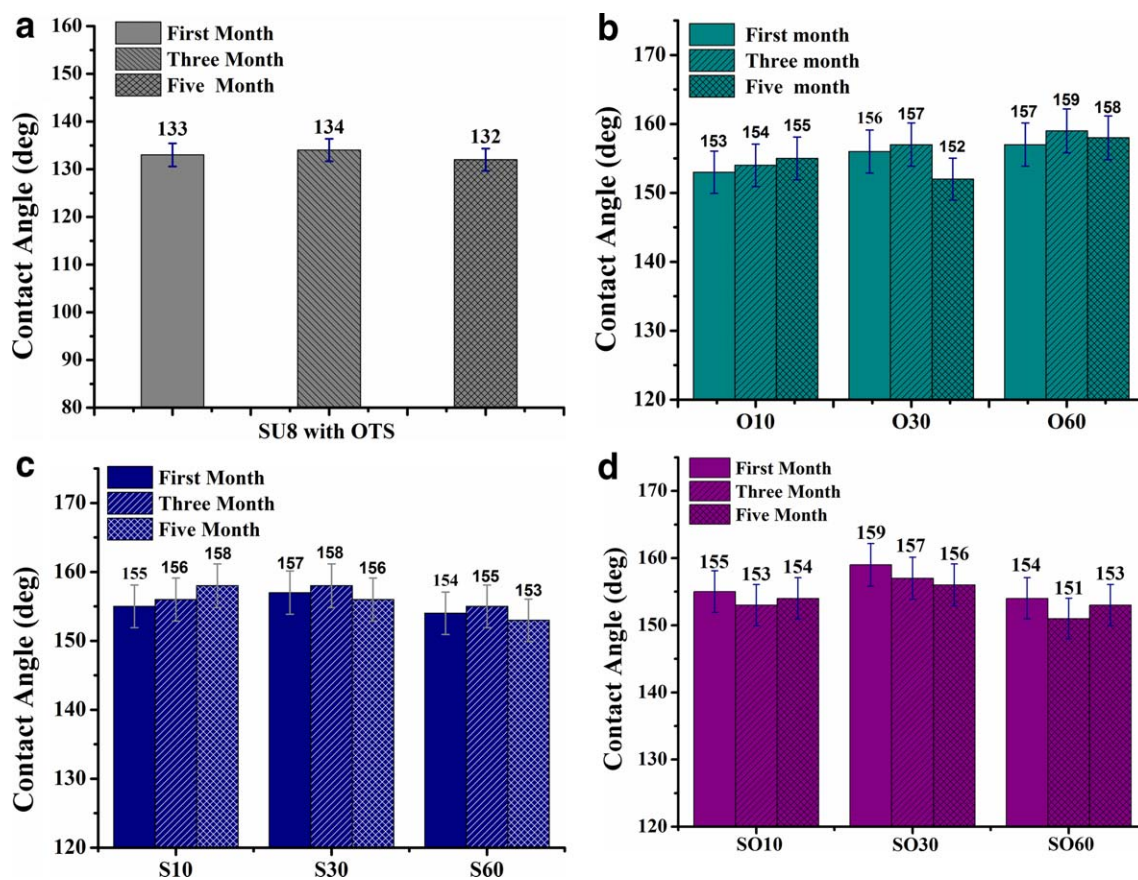


Figure 9. Stability behavior of OTS modified plasma treated SU8 surface with time (a) bare SU8, (b) O₂ plasma, (c) SF₆ plasma, and (d) SF₆ + O₂ plasma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SF₆ plasma treated SU8 for sample SO10 and SO30 shown in Supporting Information Figure S2(c) with SO60 sample. The rms roughness changed from 0.234 nm of untreated SU8 to 0.457, 0.682, and 1.2 nm with for plasma treatment time duration of 10, 30, and 60 s, respectively, as shown in Figure 2(b3). The surface roughness achieved with SF₆ + O₂ plasma is less in comparison to when treated with oxygen. Obviously, the plasma treatment for 60 s makes the SU8 surface rougher in comparison to other time durations. The wetting behavior of SU8 surface obtained after SF₆ + O₂ treatment are illustrated in Figure 3(a3). We found that, the combination of plasma (SF₆ + O₂) enables achievement of WCA $62.6^\circ \pm 2^\circ$, $65.6^\circ \pm 2^\circ$, and $69.6^\circ \pm 2^\circ$ with treatment time variation and remained hydrophilic presented in Supporting Information Figure S3(c). As compared to O₂ plasma treatment the value of WCA increased but remained lower in comparison with SF₆ plasma.

Chemical Behavior of Plasma Treated SU8 Surface. To understand the variation in WCA from surface chemistry point of view we analyzed the sample with FTIR and Raman to examine the changes in chemical properties of SU8 surface before and after plasma treatment. The third set of prepared sample was used for study of the chemical behavior of SU8 surface. The FTIR measurements were carried out in transmission mode. Polymerized SU8 surface was used as a reference sample for measurements. Figure 6(a) shows the FTIR spectra for plasma treated SU8 surface. The peak at 600 cm^{-1} and $1300\text{--}1680\text{ cm}^{-1}$ were assigned to C—C stretching of cis and trans epoxy group, respectively. The intensity of C—O and C=O stretching characteristics of because of the presence of phenol group in SU8. The peak intensity of C—S that is situated at 1050 cm^{-1} confirms the presence of photo acid generator. It can be seen from the spectra that the peak exits at $1000\text{--}1300\text{ cm}^{-1}$, which is due to formation C—O—C bond of ether after polymerization. It is also observed from spectra that after oxygen plasma (O60) treatment [refer Figure 6(a2)] no major change appeared in the peak values when compared with untreated SU8. The presence of C—O and C=O bond after oxygen plasma treatment make the surface hydrophilic. The results further indicate that in case of plasma treatment with SF₆ + O₂ (SO60) and SF₆ (S60), minor changes were observed at peak location $1300\text{--}1350\text{ cm}^{-1}$ for 60 s of plasma treatment. The peak C—C, C—H, and C—O disappeared from the spectra as illustrated in Figures 6(a3) and 6(a4) for SF₆ (S60) and SF₆ + O₂ (SO60), respectively. The relevant peak details of FTIR without OTS SAM are given in Table S1, Supporting Information. The FTIR results were thereafter verified with Raman spectroscopy. The Raman spectra for untreated SU8 and plasma treated SU8 are shown in Figure 7(a). The presence of C—O—C, C—C, and C—S bands are also observed from the Raman spectra peaks. The C—S bond, which is due to photo acid generator in SU8 at $738\text{--}762\text{ cm}^{-1}$ [Figure 7(a1)] disappeared after plasma treatment. The extra bond of CH₂ and CH₃ are observed at location of $1420\text{--}1465\text{ cm}^{-1}$ as illustrated in Figure 7(a2–a4) for O60, S60, and SO60, respectively. The presence of methyl group (CH₃) may be cause of hydrophobicity of the surface. It can be concluded that, the FTIR and Raman spectra together confirms the peaks of chemical structure present on

SU8 surface before and after plasma treatment and indicates the cause of hydrophobicity due to presence of methyl group. The peak details of Raman spectra of without OTS SAM SU8 sample are given in Table S2, Supporting Information.

Wetting Behavior of Plasma Treated SU8 Surface

The plasma treated SU8 surface were further modified with depositions of OTS self assembled monolayer. The OTS is employed as a hydrophobic material to reduce the surface energy. The plasma treated SU8 surface after deposition of OTS SAM made the surface superhydrophobic. It was found that the surface roughness increased after the OTS SAM deposition because of formation of islands on the surface. The rms roughness increased unmodified SU8 surface (0.234 nm) to 9.7 nm after OTS SAM modification shown in Figure 4(b) and corresponding surface topography are shown in Supporting Information Figure S4(b) with schematic diagram of process flow of OTS SAM deposition [Supporting Information Figure S4(c)]. The surface roughness for 60 s plasma treatment with OTS deposition is shown in Figure 4. The water contact angle of SU8 also increased significantly from $90^\circ \pm 2^\circ$ to $133^\circ \pm 2^\circ$ with OTS SAM [Figure 3(b) and Supporting Information Figure S4(a)].

Oxygen (O₂) Plasma with OTS Modification. The rms roughness value of OTS deposited on O₂ plasma treated SU8 increased to 15.7, 19.6, and 17.7 nm as illustrated Figure 4(b1). The change in roughness can be seen from surface topography for O60 from Figure 4(a1). The change in surface roughness for O10 and O30 sample are presented in Supporting Information Figure S5(a). Oxygen plasma treated SU8 surfaces were hydrophilic but after OTS deposition, the WCA increased significantly to $153^\circ \pm 2^\circ$, $156^\circ \pm 2^\circ$, and $157^\circ \pm 2^\circ$ for plasma treatment time duration 10, 30, and 60 s as shown in Figure 3(b1) and Supporting Information Figure S6(a), respectively. The surfaces obtained were superhydrophobic. A 60 s plasma treatment gives higher WCA but not much variation was obtained as compared to other plasma treatment time durations. It can be concluded, that the hydrophobicity can be improved by treating the SU8 even for 10 s plasma treatment duration with OTS deposition.

Fluorine (SF₆) Plasma with OTS Modification. The plasma treatment with SF₆ plasma does not make much change in the surface roughness but make the surface hydrophobic as is clear from the discussion in last section. The change in value of roughness after OTS SAM are 12.7, 21.0, and 21.6 nm and are illustrated in Figure 4(b2) with different time duration of plasma treatment. The corresponding surface topography are shown in Figure 4(a2) and Supporting Information Figure S5(b). The WCA after OTS SAM deposition increased significantly for such hydrophobic surface. The observed values of WCA were $155^\circ \pm 2^\circ$, $156^\circ \pm 2^\circ$, and $154^\circ \pm 2^\circ$ for different plasma treatment durations and are shown in Figure 3(b2) and Supporting Information Figure S6(b). Obviously, the rms roughness of surface also increases because of formation of islands on the surface after OTS depositions shown in surface topography images shown in Figure 4(a2). We achieved superhydrophobic surface with OTS SAM depositions even with minimum roughness after SF₆ plasma treatment.

Fluorine (SF₆) and Oxygen (O₂) Plasma with OTS Modification. The plasma (SF₆+O₂) treatment increased the rms roughness as compared to oxygen plasma. The rms roughness value of OTS SAM deposited on plasma treated SU8 also increased to 15.4, 12.1, and 13.1 nm as shown in Figure 4(b3) and Supporting Information Figure S5(c). And, the measured WCA increased in similar manner to superhydrophobic range after deposition of OTS SAM. The WCA after OTS SAM on plasma (SF₆+O₂) treated surface increased from 133° ± 2° (SU8) to 155° ± 2°, 157° ± 2°, and 153° ± 2° and are shown in Figure 3(b3) and Supporting Information Figure S6(c). The contact angle value for SO10 and SO30 is higher than the SO60 and may be due to change in the rms roughness values. All plasma treated OTS modified surfaces though shows superhydrophobic behavior of SU8 surface.

Contact Angle Hysteresis

The contact angle hysteresis was measured by measuring the advancing and receding angles by adding and removing the 2 μ L volume of water as shown in Figure 5. The Figure 5(a) shows the sequence of advancing angle from Figure (a1–a4), whereas Figure 5(b) shows the sequence of receding angle from Figure (b1–b4). The contact angle hysteresis is about 5° ± 1° for oxygen plasma treated surface whereas for SF₆ and SF₆+O₂ plasma the surface the hysteresis was about 3° ± 1°. The surface exhibited an extremely low sliding angle for the water droplet of 5 μ L. A water droplet of 5 μ L rolled off when it was gently tilted. From the rolling of behavior, it can be concluded that the surface is highly superhydrophobic surface.

Chemical Behavior of OTS SAM Modify Plasma Treated SU8 Surface. The chemical properties of SU8 film after OTS SAM on plasma treated were examined using the fourier-transform infrared (FTIR) and peaks were confirmed with Raman spectroscopy. The bare SU8 sample with OTS modification is used as a base sample for FTIR measurements. The FTIR spectra of after OTS SAM deposited untreated SU8 and plasma treated SU8 surfaces are shown in Figure 6(b). The main spectra of interest at peak location 2844, 2948, and 2990 cm⁻¹ are due to stretching of C–H group and are observed in spectra as shown in Figure 6(b1). The identical peak positions of C–H are observed in all other three plasma treated SU8 as were present in untreated SU8. After oxygen plasma (O60) treatment [Figure 6(b2)], SF₆ (S60) plasma treatment (Figure 6(b3)) and SF₆ + O₂ (SO60) plasma treatment [Figure 6(b4)] no major changes are visible in the peak values when compared with untreated SU8. Similarly, the observed peak at frequency 3014 and 3083 cm⁻¹ are stretching peak of =C–H in all OTS SAM deposited untreated and treated SU8 surfaces. The peaks from FTIR are confirmed by the Raman spectra in Figure 6(b). The Raman spectra for oxygen plasma (O60) treated SU8 are shown in Figure 7(b2), SF₆ (S60) plasma treated are shown in Figure 7(b3) and SF₆ + O₂ (SO60) plasma treated are shown in Figure 7(b4). There are no changes observed after OTS depositions on untreated and plasma treated SU8 surface on chemical bonding on the surfaces. The details of relevant peak of FTIR and Raman with OTS SAM deposited SU8 surface presented in Tables S1 and S2, Supporting Information, respectively.

XPS Spectra. Figure 8 compares the XPS scans of the untreated and plasma treated SU8 surfaces with an OTS SAM modification. The XPS of SU8 surfaces were performed with a Kratos Axis Ultra DLD with monochromatic AlK α excitation (1486.6 eV). The sample surfaces were etched by argon ion source to eliminate the surface contamination. The XPS spectra of the OTS SAM modified untreated SU8 surface are nearly identical to plasma treated OTS modified SU8 surface as in Figure 8. The surface shows significant peaks at 550 eV correspond to O-1s, Sb-3d, and 280 eV corresponding to C-1s peak, respectively. The Peak C-1s at 280 eV implies that much thicker hydrocarbon layer form on the SU8 surface. The intensity of the peak of C-1s is higher in SU8 and O60 as compared to S60 and SO60 as shown in Figure 8(a) and the relative intensity of O-1s and Si-2p peaks also higher as compared to S60 and SO60 as illustrated in Figure 8(a1,a2) for SU8 and O60. The peak at 690 eV is confirms the presence of fluorine after fluorine plasma (SF₆) treatment and is illustrated in Figure 8(a3,a4) for S60 and SO60 samples, respectively.

The XPS spectra observed for the OTS SAM modified untreated and plasma treated SU8 surface are shown in Figure 8(b). The identical peaks were observed for the plasma treated OTS SAM modified SU8 surface. It is observed that the intensity of Si-2p peak is higher in OTS SAM modified surface as compared to OTS SAM unmodified surface. The intensity of the peaks for C-1s and O-1s for SU8 and O60 as in Figure 8(b1,b2) are similar to S60 and SO60. The Peak at location 690 eV for fluorine is also observed in OTS SAM modified SU8 surface S60 and SO60 and are shown in Figure 8(b3,b4), respectively. There is no evidence for the Chlorine (Cl) peaks from OTS modified surfaces which indicate complete hydrolysis of the OTS SAM.

Stability Study of OTS SAM Modify Plasma Treated SU8 Surface

The hydrophobic durability of OTS modified plasma treated surface was monitored by measuring the WCA after several months. Out of the three set of prepared samples, two sets were used for investigations of the stability of monolayer on plasma treated SU8 surface. After OTS surface modification the WCA measurements of same set of samples were measured after a period of three months and five months. The monitored contact angle on modified SU8 surface with mentioned period are shown in Figure 9. After three months, there is not much change in WCA of untreated SU8 as is clear from the measured results shown in Figure 9(a) and for all three plasma treated surfaces as illustrated in Figure 9(b) for O₂ Plasma, Figure 9(c) for SF₆ plasma and Figure 9(d) for SF₆+O₂ plasma. The WCA of OTS modified oxygen plasma treated sample had shown a minor change after five month [refer Figure 9(b)]. The WCA for O60 changed from 158° to 152° [Figure 9(b)] but still remained superhydrophobic. Whereas, OTS modified fluorine base plasma treated SU8 gives the stable WCA values with variation of $\pm 2^\circ$ as and are shown in Figure 9(c) for SO plasma and 9(d) for SF₆ plasma.

CONCLUSIONS

This work explores the utilization of a combination of plasma treated SU8 and OTS SAM mask-less fabrication of

superhydrophobic surfaces. The effects of plasma on wetting behavior of SU8 were investigated. It was shown that, the functionalization of OTS SAM with plasma treated SU8 surface significantly improves the hydrophobicity of SU8 resulting into a superhydrophobic behavior with WCA $>150^\circ$. The change in wetting properties after OTS SAM on plasma treated surface gives the importance of surface roughness. It was found that, the plasma treatment time for 10 s is enough to improve the wetting behavior. The combination of plasma treated SU8 and OTS monolayer give the stable superhydrophobic surfaces which were confirmed by monitoring the WCA for a long period of five months. The chemical behavior of SU8 was observed by FTIR, Raman, and XPS spectra of the prepared SU8 surfaces. The SU8 is extensively used polymer in MEMS and microfluidics application, and superhydrophobic SU8 surfaces have great potential in microfluidics applications.

ACKNOWLEDGMENTS

This work was carried out at Nanomaterials and National MEMS design Centre, BITS-Pilani, India. The Author's thanks Centre for Excellence (CEN), Indian Institute of Technology, Bombay, for their support in providing the facility for characterization.

REFERENCES

- Lipowsky, R.; Lenz, P.; Peter, S. *J. Colloid Surf. Interface* **2002**, *161*, 3.
- Gao, L.; Thomas, J. *Langmuir* **2009**, *25*, 14100.
- Liu, J.; Feng, X.; Wang, G.; Wen, Y. S. *J. Phys. Condens. Matter* **2007**, *19*, 356002.
- Xiu, Y.; Zhu, L.; Hess, W.; Wong, C. P. *Nanoletters* **2007**, *7*, 3388.
- Li, X.; Tay, B.; Miele, P.; Brioude, A.; Cornu, D. *J. Appl. Surf. Sci.* **2009**, *255*, 7147.
- Morgan, M.; Robert, E.; John, C.; Lambert, R.; Gimpsey, M. *J. Colloid Interface Sci.* **2012**, *367*, 502.
- Tropmann, A.; Tanguy, L.; Koltay, P.; Zengerle, R.; Riegge, L. *Langmuir* **2012**, *28*, 8292.
- Ma, Y.; Cao, X.; Feng, X.; Ma, Y.; Zou, H. *J. Polymer* **2007**, *48*, 7455.
- Chibowski, E.; Hołysz, L.; Terpilowski, K.; Jurak, M. *J. Colloid Surf. A: Phys. Eng. Aspects* **2006**, *291*, 181.
- Kumar, V.; Sharma, N. N. In *Micro and Smart Devices and Systems*; Vinoy, K. J.; Ananthuresh, G. K.; Partap, R.; Krupanidhi, S. B.; Springer: India, **2014**; Chapter 16, pp 265–283.
- Kumar, V.; Bhat, K. N.; Sharma, N. N. *J. Adhes. Sci. Technol.* **2014**, *29*, 308.
- Abgrall, P.; Conedera, V.; Camon, H.; Gue, A. M.; Nguyen, N. T. *Electrophoresis* **2007**, *28*, 4539.
- Sikanen, T.; Tuomikoski, S.; Ketola, A.; Kostianen, R.; Franssila, S.; Kotiaho, T. *Lab Chip* **2005**, *5*, 888.
- Kumar, V.; Sharma, N. N. *J. Nano* **2012**, *2012*, 1.
- Sato, H.; Matsumura, H.; Keino, S.; Shoji, S. *J. Micromech. Microeng.* **2006**, *16*, 2318.
- Keller, S.; Blagoi, G.; Lillemose, M.; Haefliger, D.; Boisen, A. *J. Micromech. Microeng.* **2008**, *18*, 125020.
- Campo, A.; Greine, C. *J. Micromech. Microeng.* **2007**, *17*, 81.
- Joshi, M.; Pinto, R.; Rao, V. R.; Mukherji, S. *J. Appl. Surf. Sci.* **2007**, *253*, 3127.
- Zhao, J.; Sheadel, A.; Xue, W. *Sensor Actuat. A: Phys.* **2012**, *187*, 43.
- Walther, F.; Polina, D.; Stefan, Z.; Kaiser, M.; Herberg, H.; Gigler, A.; Stark, R. W. *J. Micromech. Microeng.* **2007**, *17*, 524.
- Rasmussen, K. H.; Keller, S.; Jensen, F.; Jorgensen, M.; Hansen, O. *J. Micromech. Microeng.* **2013**, *112*, 35.
- Chung, C. K.; Hong, Z. *J. Micromech. Microeng.* **2007**, *17*, 207.
- Walther, F.; Drobek, T.; Gigler, M. A.; Hennemeyer, M.; Kaiser, M.; Herberg, H.; Shimitsu, T.; Morfill, E.; Stark, R. W. *Surf. Interface. Anal.* **2010**, DOI: 10.1002.sia.3515.
- Velasco, M. J.; Vlachopoulou, M.; Tserepi, A.; Gogolides, E. *J. Micromech. Eng.* **2010**, *87*, 782.
- Hong, G.; Holmes, A. S.; Heaton, M. E. *J. Microsyst. Technol.* **2004**, *10*, 357.
- Shirtcliffe, N. J.; Aqil, S.; Evans, C.; McHale, G.; Newton, M.; Perry, C.; Roach, P. *J. Micromech. Microeng.* **2004**, *14*, 1384.
- Yoon, Y.; Lee, W.; Lee, J. B. *J. Micromech. Microeng.* **2012**, *22*, 035012.
- Park, S. G.; Moon, J. H.; Jeona, H. C.; Yang, S. *J. Soft Matter* **2012**, *8*, 4567.
- Gooding, J.; Mearns, F.; Yang, W.; Liu, J. *Electroanalysis* **2003**, *15*, 81.
- Haensch, C.; Hoeppener, S.; Schubert, S. *Chem. Soc. Rev.* **2010**, *39*, 2323.
- Glass, N. R.; Tjeung, R.; Chan, P.; Yeo, Y.; Friend, R. *J. Bio-microfluidics* **2011**, *5*, 036201.