Tailoring the surface topography and wetting properties of oxygen-plasma treated polydimethylsiloxane

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In this work, we address the issue of controlled modification of the surface topography of polydimethylsiloxane (PDMS) when subjected to oxygen-based plasma treatments, and we investigate the resulting enhanced surface area as a means of controlling the surface wetting properties. We fabricate wavy structures of controllable *nanoscale* amplitude and periodicity in the range 50–300 nm, spontaneously formed on PDMS surfaces, by means of appropriate plasma processing conditions and radiation pretreatment. Such structures are desirable for applications in sensor microdevices, the development of biocompatible materials, and micro- and nanosystems in general. Ordered structures fabricated on polydimethylsiloxane of relatively high amplitude and small periodicity are chosen as appropriate surfaces for the enhancement of the surface wetting properties, which can be tuned from highly hydrophilic to hydrophobic when combined with a hydrophobic coating applied on the rich surface nanotexture. This fact underlines the potential application of the proposed technique in the field of microfluidics, where polydimethylsiloxane is gaining popularity as structural material for microfluidic devices. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2136421]

I. INTRODUCTION

Interfacial properties of polymers and their control become important at submicrometer scales, as polymers find widespread applications from micro- and nanoelectronics to optoelectronics, microelectromechanical systems, microfluidics, and biomaterials. Since roughness or in general the topography of surfaces often results from processing, deposition and etching[1–3] are extensively examined as processes tailoring the surface properties. Growth of uniformly distributed surface undulations in homopolymer thin films has been recently observed and attributed to the dewetting of very thin films as they deposit on solid substrates.[4,5] In addition, growth of similar surface undulations has been observed on thick elastomeric substrates and it has been attributed to the mismatch of thermal-expansion coefficients between a stiff layer and a thick elastomeric substrate.[6–9] In Refs. 7 and 9, the formation of complex and ordered structures has been observed on oxygen-plasma treated, thermally crosslinked, bulk (10–35-mm thick) polydimethylsiloxane (PDMS), and the observed periodicities were in the micrometer range.

The present work addresses the issue of intentional and controllable modification of surface topography of thin (in the μm range) and radiation curable (as opposed to thermally curable[7–9]) PDMS films and the fabrication of ordered structures on PDMS with periodicity for the first time in the sub-half-micrometer range, induced by plasma treatment of PDMS, crosslinked at different degrees. In specific, the control of the surface roughness and periodicity on PDMS by the electrode temperature and the radiation exposure dose (crosslink density) of the polymer are presented. In addition, the effect of surface topography modification on the wetting

properties of the treated PDMS surface is investigated. We show that these ordered structures on PDMS surfaces, especially those characterized by relatively high roughness amplitude and small periodicity, enhance the surface wetting properties that can be tuned from highly hydrophilic to hydrophobic with the application of hydrophobic coating (PTFE) on such a surface.

Since control of the PDMS surface topography is reliably achieved, as will be shown below, the ability easily to create structures with wavelength in the sub-half-micrometer scale and amplitude in the nanometer scale is established, with potential applications in the expanding field of micro- and nanofabrication. Furthermore, control on the surface wetting properties that is achieved in this work by means of nanotexturing the PDMS surface in the plasma can find potential applications in the field of microfluidics for controlling fluid transport properties in microchannels built in PDMS.

II. MATERIALS AND METHODS

Commercial PDMS material from Aldrich (pure PDMS of M_n=60 000 and M_W=120 000) and from UCT (94.5% PDMS, copolymer 5% diphenyl siloxane, copolymer 0.5% methyl-vinyl-siloxane, of M_n=450 000 and M_W=990 000) were used. The former material is easily crosslinked with e-beam exposures, while the latter is photosensitive and crosslinkable with deep ultraviolet (UV) radiation (in the range 200–250 nm). Thin films were prepared by spin-coating a solution of PDMS in methyl-isobutyl ketone (MIBK), to form a 80-nm-thick film on top of 360 nm hard-baked novolac resist (AZ5214 of Clariant), coated on a Si

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wafer. Subsequently, the samples were exposed to crosslink radiation and developed in MIBK to remove non-crosslinked areas. The samples were then treated in oxygen plasmas generated either in a reactive ion etcher (RIE) from Nextral (NE 330) or in an inductively coupled (ICP) plasma reactor from Alcatel (Micromachining Etching Tool, MET). In the case of the ICP plasma reactor, the temperature of the electrode was well controlled, and a good thermal contact of the samples with the electrode was provided by means of He flowing on the back side of the samples to thermally equilibrate the samples to the electrode temperature. In the RIE reactor, on the contrary, samples are placed on a thick quartz plate, preventing efficient heat conduction from the samples, and thus the temperature of a treated surface can easily exceed 100 °C within 1 min after plasma ignition.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to generate surface images and to quantify roughness, while statistical analysis is performed on the resulting images to yield the scaling behavior of surface roughness (SR). Samples treated in oxygen plasmas were analyzed by either a Nanoscope III Digital Instruments (in the tapping mode) or by a Topometrix TMX 2000 AFM instrument (in the contact mode).

The effect of the topography modification on the wettability of the surface was examined by water contact angle measurements. PDMS surfaces of plasma-modified topography were used as is or spin-coated with a commercial Teflon-like polymer (AF1600 from Dupont) to yield hydrophobic surfaces. In order to minimize alteration of the surface topography by the coating, a thin film of AF1600 (10–20 nm) was used. The film homogeneity was checked by AFM measurements and by contact angle hysteresis measurements. A small roughness (0.6 nm rms value) and a relatively small hysteresis (11°) were found, indicating a film of a homogeneity not very different from that of a much thicker film. The effect of surface topography on the surface wettability was investigated by water contact angle measurements (in static and dynamic mode) on a DIGIDROP system from GBX.

III. RESULTS AND DISCUSSION

A. Surface topography modification and surface analysis

We claim that PDMS surface topography can be controlled in two ways: (a) at constant RIE treatment time, by varying the radiation exposure dose (crosslink density), and (b) at constant crosslink density, by varying the temperature of the sample in an ICP reactor with good heat transfer.

Figure 1 shows AFM images of PDMS surfaces after treatment in O_2 plasmas. Images in (a)–(d) correspond to samples treated for 1 min in a RIE reactor after being exposed to variable radiation dose. It is obvious from these images that O_2 plasma-treated PDMS surfaces acquire topography of increasing roughness with increasing exposure dose. The top-down image of the surface in Fig. 1(d) indicates strongly a periodic surface roughness of random orientation. Periodic roughness is found also on the surfaces shown in Figs. 1(a) and 1(b), however of smaller magnitude

and periodicity. In fact, comparison of the images in Fig. 1 indicates an increase of roughness and periodicity with exposure dose.

To describe in detail the modification of the surface topography of plasma-treated PDMS surfaces, all acquired AFM images were statistically analyzed and valuable information was obtained concerning the type of roughness and its properties. The analysis is based on the height-height correlation function $G(r)$,[10] whose behavior determines the character of surface roughness. In the case of self-affine roughness,[10,11] $G(r)$ follows a power law up to a distance called the correlation length r_{cor} and then stabilizes to a value related to the surface roughness w (rms value) as $G(r > r_{cor}) = \sqrt{2}w$. However, when the surface exhibits a quasiperiodic structure, at values of $r > r_{cor}$, $G(r)$ exhibits an oscillatory behavior about the value of w. The first minimum of the oscillatory behavior determines the characteristic wavelength λ of the quasiperiodic surface. Figure 2 shows the surface correlation functions $G(r)$ for a series of PDMS samples treated for 1 min in the RIE O_2 plasma after being exposed to variable radiation dose. As we can see, except from the $G(r)$ for the surface with the smallest dose shown (at which PDMS is weakly crosslinked and thus totally removed from the novolac substrate surface as it dissolved in MIBK), all other surfaces exhibit clearly an oscillatory behavior demonstrating the periodic character of the surface roughness for these doses. The values of λ at various doses, estimated from the first minima of the corresponding $G(r)$, are shown as labels on the curves, while the exact dependence of λ and of the corresponding surface roughness w on the exposure dose is shown in Fig. 3. An increase of roughness and wavelength is indicated with increasing exposure dose, while the observed roughness saturation can be possibly attributed either to the small PDMS thickness (~80 nm) or to the saturation of the crosslinking of the PDMS induced by radiation pretreatment. Figure 3 demonstrates that such radiation pretreatment of the PDMS surface followed by O_2 plasma treatment allows control of the surface topography, with roughness amplitude ranging in the nanoscale and periodicity in the sub-half-micrometer scale.

A similar effect on the surface topography was also observed for samples, crosslinked by UV radiation of the same dose, and then treated for 2 min in the ICP reactor at different electrode temperatures. Statistical analysis based on the height-height correlation function $G(r)$ of images obtained on PDMS surfaces treated at increasing electrode temperature yields the results shown in Fig. 4. Here, the increased processing temperature increases the surface roughness while its periodicity stays relatively constant.

B. Explanation of the controlled topography modification

The topography shown in Fig. 1 is similar to "spinodal dewetting" formations in very thin (<10 nm) polymer films on solid substrates,[4,5] or to the spontaneous formation of buckles in stiff thin films on elastomeric substrates, due to the mismatch of their thermal-expansion coefficients.[6–9] A simple calculation of the stress due to van der Waals forces[5]
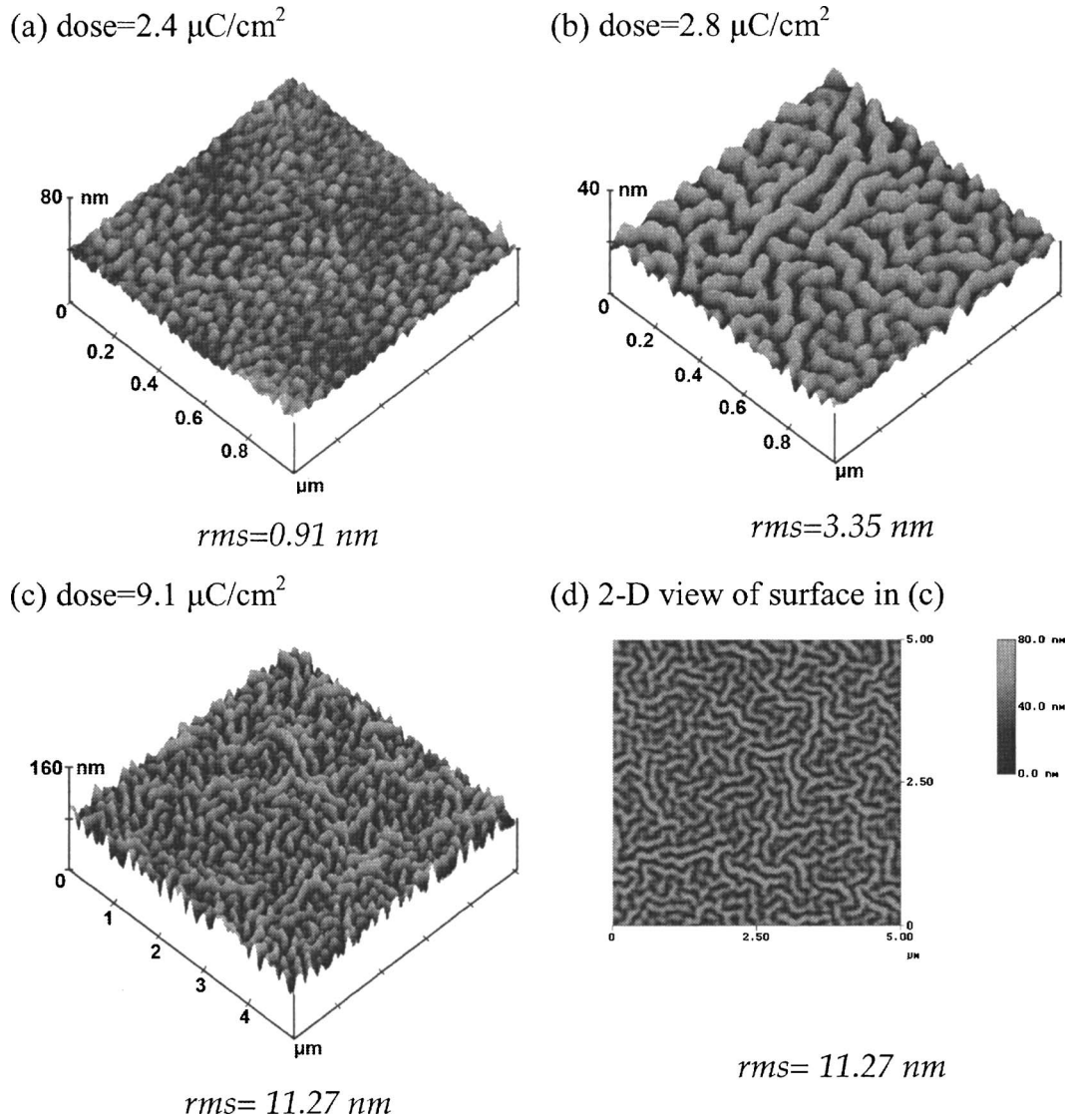
(a) dose=2.4 μC/cm^2

(b) dose=2.8 μC/cm^2

rms=0.91 nm

rms=3.35 nm

(c) dose=9.1 μC/cm^2

(d) 2-D view of surface in (c)

rms= 11.27 nm

rms= 11.27 nm

FIG. 1. AFM images of O_2-plasma treated PDMS surfaces in a RIE reactor after being exposed to different radiation doses (a)–(d). For (a) and (b) images a 1×1 μm^2 scan area was used, while in (c) and (d) a scan area of 5×5 μm^2 is shown.

(the driving force for spinodal dewetting) and of the stress due to the mismatch of the thermal-expansion coefficients[9] shows that the latter exceeds the former immensely, by five orders of magnitude. Given the temperature increase during plasma treatments, the latter mechanism is more plausible. In agreement with this, the formation of similar periodic wavy structures on O_2 plasma-treated bulk PDMS samples, reported in Refs. 7 and 9, has been attributed to the relief of the compressive stress by the buckling of the thin silica-like layer that is formed on the PDMS surface as a result of the plasma treatment. In more detail, the thin silica layer is formed on the PDMS surface at a temperature that usually exceeds ambient temperature in plasmas, due to heat transferred from ions of the discharge to the treated surface. Thus silica is usually formed on a thermally expanded polymer, and compressive stress grows during subsequent cooling of the sample to room temperature as a result of mismatched thermal-expansion coefficients for silica and PDMS. Similar spontaneously formed ordered structures have been observed on PDMS samples after metal deposition by thermal

evaporation.[6,7] The model used for describing the phenomenon considers a stack structure consisting of a top hard layer (THL) and a bottom soft underlayer (BSL) and it expresses the compressive stress developed in the unbuckled film[6,9] as a function of the properties of the two layers

$$\sigma = E_{THL}(\alpha_{BSL} - \alpha_{THL})\Delta T/(1 - \nu_{THL}), \tag{1}$$

where E_{THL} is the Young modulus of the top hard layer (silica in our case), $(\alpha_{BSL}-\alpha_{THL})$ is the thermal-expansion coefficient mismatch between the top hard layer and the underlayer, ΔT is the temperature drop of the structure after completion of the plasma treatment, and ν_{THL} is Poisson's ratio of the top layer. As the temperature drops from the processing temperature to room temperature, the buckling phenomenon appears to relieve the built-up stress. The periodicity λ of the associated sinusoidal wave pattern is given by[6–9]
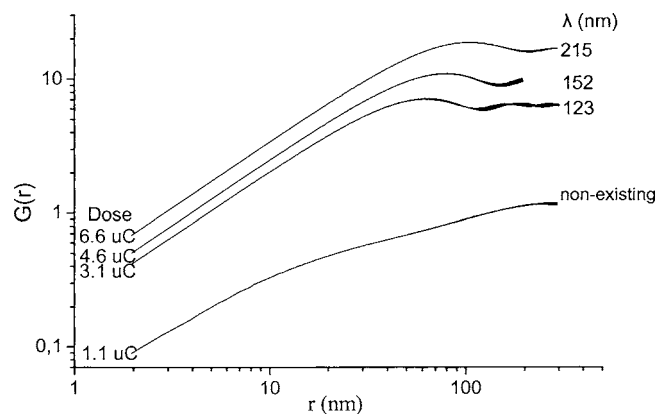
FIG. 2. Scaling analysis of AFM images of O_2-plasma-treated PDMS surfaces, based on the height-height correlation function $G(r)$. The correlation function for four surfaces exposed to different doses (from 1.1 to 6.6 $\mu C/cm^2$) is shown and the values of periodicity (wavelength) obtained from this analysis are indicated.

$$\lambda \approx 4.4 t_{THL}[E_{THL}(1 - \nu_{BSL}^2)/E_{BSL}(1 - \nu_{THL}^2)]^{1/3}, \qquad (2)$$

where t_{THL} is the thickness of the top hard layer. According to Eqs. (1) and (2), the built-up compressive stress and the resulting roughness width are determined by ΔT, while the periodicity (λ) is determined solely by the thickness of the hard layer (for a certain underlayer). Therefore, our strategy for tailoring the surface topography was determined by the above-mentioned dependencies, and included control of roughness alone by tuning ΔT (see Fig. 4) and control of both periodicity (λ) and roughness (w) by tuning E_{THL} (by means of radiation pretreatment, see Fig. 3).

(i) Effect of ΔT on roughness. At a constant radiation pretreatment of PDMS samples, followed by plasma treatments of equal duration but at different electrode temperature T, roughness width is expected to increase with increasing ΔT, while λ is expected to remain relatively constant, being dependent on the thickness of the THL,[6–9] in accordance with Eqs. (1) and (2). This is demonstrated in the results shown in Fig. 4, where roughness is shown to increase with the plasma treatment temperature, while λ is found relatively unaffected by the temperature change. The thickness of the silica layer grown during O_2 plasma treatment with the electrode temperature kept at 20 °C was measured by XPS analysis and found to reach a plateau value of 4.5 nm after a few seconds treatment,[12] under the simultaneous effects of oxidation and sputtering by ion bombardment. Therefore, Eq. (2) yields for silica as THL and PDMS as BSL, $\lambda \approx 60 t_{silica}$, which in turn, for $E_{silica} = 70$ GPa, $E_{PDMS} = 20$ MPa, $\nu_{PDMS} = 0.48$, and $\nu_{silica} = 0.20$, yields a periodicity of the order of 270 nm, in reasonable agreement with the results of λ in Fig. 4. (The small increase of λ with temperature can be explained by a small variation of the silica thickness, as silica formation is kinetically favored at higher temperatures.) The periodicities observed in this work are smaller compared to those in Refs. 7 and 9, where periodicities in the range [0.5 − 10 μm] and [0.4−4 μm] were reported, respectively, due to the small value of t_{silica} (4.5 nm was determined in our work compared to 500 nm measured in Ref. 7).

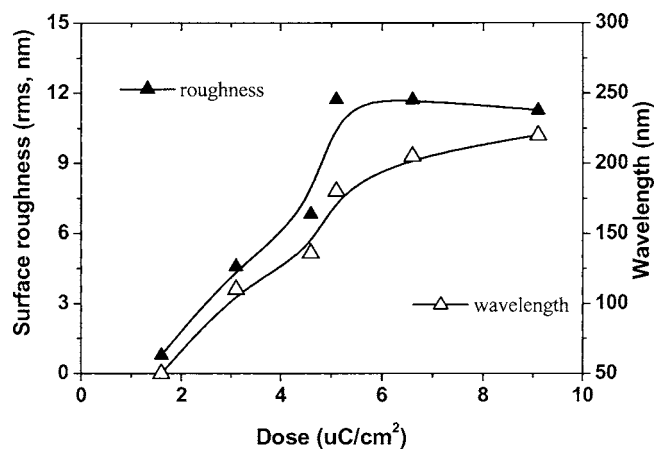*(ii) Effect of crosslinking on roughness and periodicity.*

FIG. 3. Variation of the surface roughness and periodicity of crosslinked PDMS surfaces as a function of the exposure dose. All surfaces were treated in O_2 RIE plasmas for 1 min (within 1 min, temperature increased to 70 °C for all samples), at identical conditions. The values of roughness and wavelength have been obtained from the scaling analysis based on the height-height correlation function, as in Fig. 2.

For the experiments which results are reported in Fig. 3, plasma treatment conditions and time were kept constant. Therefore, the temperature at which formation of SiO_x occurred, as well as the thickness of the grown silica layer, were the same for all surfaces examined. The observed variation of roughness and wavelength (λ) with exposure dose can only be attributed to the corresponding variation of the Young modulus of the THL. More specifically, we believe that the crosslinking induced by the radiation pretreatment of the PDMS surface modifies its Young modulus, leading to a PDMS of increased stiffness for increased radiation exposure dose. If the silica layer and the stiffened PDMS underlayer are treated as one bilayer plate on top of the novolac (AZ5214) underlayer, then the effective bending stiffness of the bilayer increases as the radiation exposure dose (i.e., crosslink density) increases, and thus the roughness and its periodicity are expected to increase, in accordance with Eqs. (1) and (2). This explains the observed simultaneous increase of surface roughness and periodicity with increasing expo-
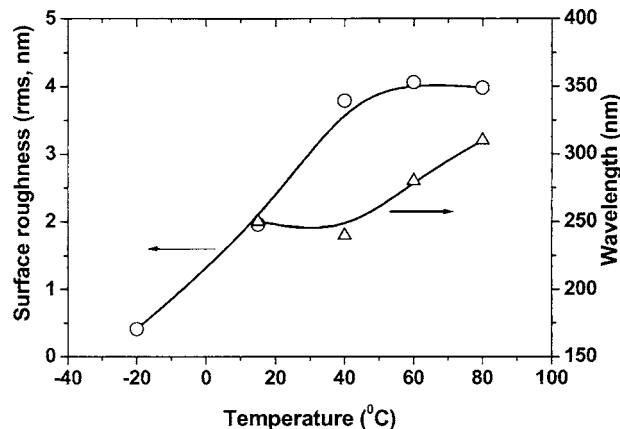

FIG. 4. Variation of surface roughness and periodicity of O_2-plasma-treated PDMS surfaces as a function of the electrode temperature (ICP reactor) at which plasma processing was effected. Other plasma conditions were maintained constant at 10 mTorr pressure, 600 W ICP plasma power, −100 V electrode bias voltage, and 2 min treatment duration.
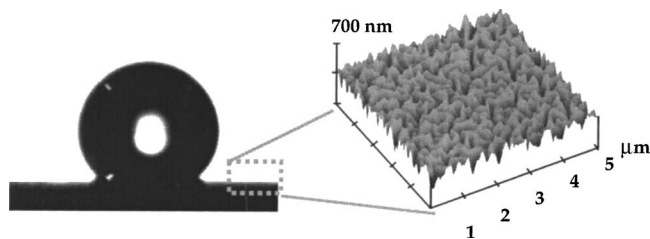
FIG. 5. A water droplet deposited on a PDMS plasma-nanotextured surface (RIE O_2 plasma treatment for 4 min), the surface topography of which is shown in detail in the AFM image.

sure dose, as shown in Fig. 3. Indeed, from the figure, a similar dependence of roughness and periodicity on exposure dose is clearly deduced. The observed increase in the wavelength of the buckles with exposure dose on O_2-plasma treated PDMS is in agreement with Ref. 7, where buckling appears in thin metal films thermally evaporated on UV patterned thick PDMS.

Although the production of rough but ordered surfaces on PDMS is the target of this work, a short comment is worthwhile for applications in which smooth surfaces are desired, for example in scaffolds for cell adhesion and proliferation:[13] we have shown recently[14,15] that surface roughness of plasma-treated PDMS can be considerably reduced by optimization of the gas processing chemistry (short pretreatment in He/SF_6 plasma followed by treatment in O_2 plasma).

C. Effect of topography modification on surface wettability

Having determined the treatment parameters (radiation exposure dose and plasma exposure conditions) affecting the PDMS surface topography in a controlled manner such that tailoring of the surface topography was possible, we aimed at the exploitation of the enhanced surface topography for modification of the surface wetting properties. It is well known that the wettability of solid surfaces is affected by both the chemical composition and the geometrical microstructuring of the surface.[16,17] For this purpose, it is desirable to obtain surfaces with a significant enhancement of the surface area, i.e., a PDMS surface with ordered roughness of small periodicity and relatively high amplitude.

To this end, a 1230-nm-thick film of PDMS, after being pretreated with a high UV radiation dose, was exposed to O_2 plasma (RIE). A significant nanotexturing of the surface was obtained, after 4 min plasma treatment, characterized by a rms roughness value of 54 nm (roughness amplitude of 345 nm) and a periodicity of 410 nm, shown in the AFM image of Fig. 5. If, in addition, a hydrophobic treatment was imposed on the surface, for example by spin-coating a very thin (10–20 nm) Teflon-like material (AF1600 from Dupont), the static water contact angle on the surface increased from $112° \pm 2°$, characteristic of a Teflon-like flat surface, to a value of $130° \pm 2°$ (shown in Fig. 5), for a Teflon-coated nanotextured PDMS surface. Actually, the contact angle is an increasing function of the treatment time in the O_2 plasma, up to a saturation level, as shown in Fig. 6(a). The increase of surface roughness as a result of the increase of the PDMS
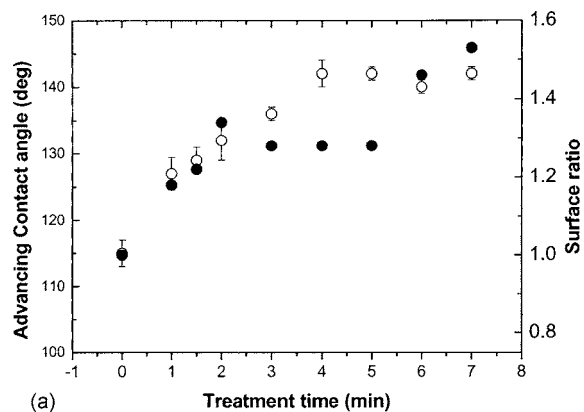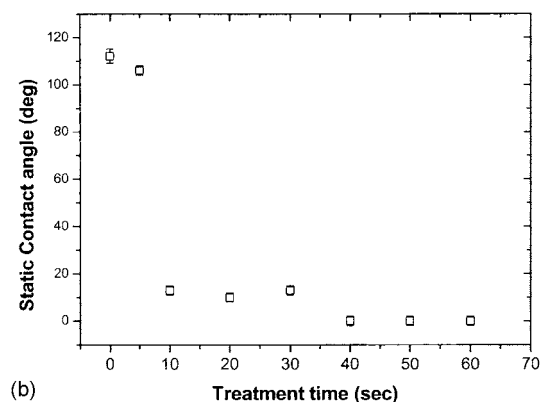
FIG. 6. Effect of plasma treatment on the PDMS surface wetting properties. (a) Increase of the advancing water contact angle (open circles) of a Teflon-like thin film (10 nm) coated on an O_2 RIE plasma-modified PDMS surface, and the corresponding increase of the effective surface area (filled circles), estimated by means of AFM measurements, with plasma treatment time. (b) Decrease of the static water contact angle of an O_2 plasma treated PDMS surface with treatment time. Plasma treatment conditions: 10 mTorr pressure, 400 W plasma power.

treatment temperature with increasing plasma treatment time can explain the apparent increase of the contact angle of the Teflon-coated surface. In fact, the maximum apparent increase of the advancing contact angle (from $115°$ to $141°$) observed in Fig. 6(a) can be attributed to an increase of the actual surface area after plasma roughening by $r \sim 1.8$ (where r is the ratio of the actual to the projected surface area), as predicted by Wenzel's formula.[16] The apparent increase of the surface area by roughening, as estimated by AFM measurements on the treated surfaces, was found to be about $r \sim 1.5$ at long treatment times (6–7 min), underestimating by little the effective surface area predicted by Wenzel's formula probably due to limited AFM resolution. In addition, the contact angle hysteresis, which distinguishes a surface in the Wenzel regime from one in the Cassie-Baxter regime,[18] was found to increase with treatment time (from around $10°$ for a Teflon-coated untreated PDMS surface to around $50°$ for a Teflon-coated 6–7 min O_2-plasma-treated surface), indicating a surface in the Wenzel regime.

Normally, a PDMS surface, after its treatment in O_2 plasmas, is transformed to a silicon-dioxide-like surface,[12,14] thus exhibiting hydrophilic properties. In fact, as is shown in Fig. 6(b), shortly after the exposure to O_2 plasmas (45 s), the static water contact angle on the PDMS surface decreases

from $112° \pm 3°$ to nearly zero, indicating complete wetting of the surface. We believe that this is the result of both the fast (within 10 s) chemical transformation (oxidization)[14] of the surface and the increasing roughening of the surface with treatment time.

The enhancement of the surface hydrophobicity or hydrophilicity, induced by the modification of the PDMS topography, can find numerous applications in the field of microfluidics, where PDMS is widely used as a structural material for microfluidic devices. Certainly in these devices, the surface topography can be appropriately modified on purpose, to induce desirable effects on the liquid transport and its dynamic tuning[19] (for example, by means of electric fields).

IV. CONCLUSION

In summary, we have shown that the surface morphology and wettability of PDMS (an example of Si-containing polymers) can be tailored on demand. In specific, the surface topography can acquire the desired magnitude of surface roughness (w) and periodicity (λ) in the nanometer- and sub-half-micrometer-scale, respectively. This is possible since, on the one hand, periodicity is solely affected by the thickness of the silica-like layer grown on plasma-treated PDMS surfaces, and on the other hand, the magnitude of roughness is determined by the difference between plasma processing and ambient temperature (for a polymer of certain history before plasma treatment). In addition, both magnitudes are affected simultaneously by varying the Young modulus of the polymer. Therefore, plasma processing parameters can be appropriately adjusted to control and yield desirable surface topography with formation of periodic structures of nanometer size. Such controlled modification of the surface of a widely used polymer such as PDMS can find numerous potential applications in the fabrication of sensor and microfluidic devices, as on the one hand it allows easy fabrication of nanometer-scale structures and on the other it affects significant surface properties, such as the effective surface area and the wettability, as we have shown here.

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