

Highly hydrophobic hierarchical nanomicro roughness polymer surface created by stamping and laser micromachining

Marcos R. Cardoso,¹ Renato J. Martins,¹ Apurba Dev,² Tobias Voss,³ Cleber R. Mendonca¹

¹Instituto de Física de São Carlos, Universidade de São Paulo, São Paulo, Brazil

²School of Information and Communication Technology, KTH Royal Institute of Technology, Electrum 229, 164 40 Kista, Sweden

³Institute of Semiconductor Technology, Braunschweig University of Technology, 38023 Braunschweig, Germany

Correspondence to: M. R. Cardoso (E-mail: cardosomr@ifsc.usp.br)

ABSTRACT: This article describes the design and fabrication of hierarchical nanomicrostructured polymer surfaces with high hydrophobicity. The nanoscale roughness is achieved by stamping a ZnO nanowire film into PDMS. Subsequently, microstructures with different periodicities are created in the stamped PDMS sample by direct laser writing using femtosecond pulses. With this approach, we were able to produce hierarchical surface morphologies, composed of nano and microscale structures that exhibit water contact angles larger than 160°. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42082.

KEYWORDS: morphology; nanostructured polymers; surfaces and interfaces

Received 12 November 2014; accepted 3 February 2015

DOI: 10.1002/app.42082

INTRODUCTION

The development of surfaces presenting high hydrophobicity has been attracting considerable attention in the last few years, aiming at applications from microfluidics to self-cleaning devices.^{1–4} Since the wettability of surfaces depends on their topology and chemical nature,^{5–9} strategies combining both aspects have been developed to obtain superhydrophobic materials.^{6,10–14} The lotus leaf is a natural superhydrophobic surface that presents a water contact angle (CA) on the order of 160°, and has inspired the fabrication of synthetic superhydrophobic surfaces. The large CA of the lotus leaf is attributed to the combined effect of its covering wax and surface structure, which presents a hierarchical structure composed of a dualscale roughening (micro and nanoscale).^{15,16} In order to transfer the lotus leaf effect to synthetic surfaces, a combination of chemical modification and patterning of the sample has been used.^{17–19} Several methods, from extruding of polymers²⁰ to femtosecond (fs) laser structuring,⁵ have been proposed to design superhydrophobic surfaces.^{1,5,6,10,12–14,19,21,22} Transferring the lotus leaf pattern to an artificial surface involves a precise control on the surface microstructuring, while keeping the nanostructure already obtained on the surface.

This article presents a hierarchical structuring process that combines stamping (nanoscale) and laser micromachining (microscale), to create highly hydrophobic surfaces with noteworthy CA with water. Such approach combines advantages of both methods, such as the flexibility for the nanoscale fabrication,

provided by stamping, and the selectivity of fs-laser micromachining. Furthermore, both methods work, in principle, for a large range of materials. By stamping, the surface pattern of a ZnO nanowires film is transferred to a polydimethylsiloxane (PDMS) film, resulting in a nanostructured PDMS surface. Subsequently, such sample is micromachined by femtosecond laser pulses to create periodic surface microstructures. With this method, hierarchical surface morphologies exhibiting water contact angle larger than 160° can be produced.

EXPERIMENTAL

Polydimethylsiloxane (PDMS) is a silicon-based organic polymer that has been widely used for the fabrication of microdevices.^{23,24} Thanks to its favorable physical and chemical properties, PDMS has been used in the production of high-quality patterns by soft-lithography.²⁵ Moreover, because PDMS is transparent in the visible and near infrared regions,²⁶ it is also a good candidate for laser microstructuring via multiphoton absorption.

PDMS films were prepared by using the Sylgard 184 elastomer kit (Dow Corning); 0.5 g of the curing agent was mixed to 5.0 g of the PDMS base into a plastic container. In order to remove the bubbles resulting from the mixing process, the PDMS mix was sonicated for 5 min and stored in a refrigerator at 5°C for 24 h. Subsequently, the uncured PDMS mix (bubble free) was cast into the desired mold and placed into an oven at 60°C for 10 h.

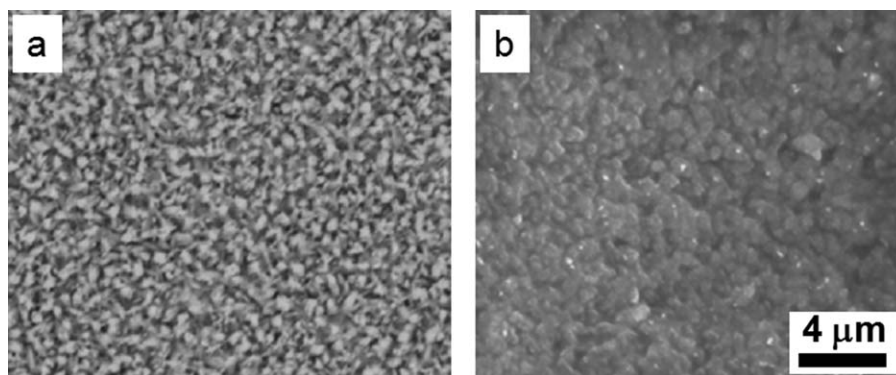


Figure 1. Scanning electron microscopy image of the ZnO nanowire film (a) and the PDMS stamped sample (b). The same scale applies to both images.

Zinc oxide (ZnO) nanowires films were obtained according to the procedure described in Ref. (27). This film was used as a nanostructured template in the mold for the PDMS. After curing, the PDMS film was gently removed from the mold, yielding a negative of the ZnO nanowire pattern.

To obtain the hierarchical structure required to achieve superhydrophobicity, nanostructured PDMS samples were microstructured by fs-laser micromachining. For this task, we used the 150-fs pulses from a Ti:Sapphire laser amplifier, operating at 780 nm with a repetition rate of 1 kHz. The micromachining process consists of focusing the laser beam, using a 0.40-NA microscope objective, on to the surface of the sample that is placed on a computer controlled three-axis stage. The stage is moved at a constant speed of 0.5 mm/s with respect to the laser beam, which allows creating the desired structure on the sample surface. The fabricated samples present very good uniformity, thanks to the consistency of stamping and laser micromachining. The maximum size of the samples we are able to fabricate in our setup is of about 4 cm². fs-laser micromachining was performed using a pulse energy of 0.5 μJ. The morphology of the samples was analyzed by scanning electron microscopy (TM 3000 Tabletop Microscope—Hitachi) and atomic force microscopy (Nanosurf easyScan 2).

The wetting properties of the samples were studied by measuring the static contact angle (CA) for water, using a goniometer coupled to a horizontal microscope (KSV CAM 200). The CA measurements were performed at 25°C and relative air humidity around 40%. Water droplets with a volume of about 3 μL (radius of approximately 1 mm), were used for all measurements.

RESULTS AND DISCUSSIONS

Figure 1(a) shows a scanning electron microscopy (SEM) image of a ZnO nanowires film that was used as a nanostructured mold for

the PDMS sample. The micrograph displays the high aspect ratio of the ZnO nanowires film surface. Figure 1(b) shows the SEM image of the nanowire pattern (negative) transferred to PDMS, according to the method described above. As it can be seen, the nanostructured pattern obtained in PDMS presents a rounder aspect than the original ZnO nanowires film [Figure 1(a)].

The morphology of the ZnO nanowires film and the pattern obtained in PDMS (negative) can also be observed in the atomic force micrographs, shown in Figure 2. The atomic force microscopy (AFM) image of the nanowires film displays spikes distributed along the sample [Figure 2(a)], while for the PDMS sample, obtained by stamping, a surface pattern with a rounder morphology is observed. From the atomic force micrographs we determined the surface roughness (arithmetic average—*R_a*), obtaining a value of 80 nm for both samples. This result indicates that the stamping process allowed obtaining a nanopatterning on the PDMS sample with the same general features of the mold (ZnO nanowires film).

The nanostructured PDMS sample, obtained by stamping, was micromachined using the fs-laser system described above, to obtain a hierarchical surface structuring. The micromachining conditions determined as optimal for PDMS are pulse energy of 0.5 μJ and scanning speed of 0.5 mm/s. We produced periodic surface microstructures composed of pillars with squared cross-sections, with periodicities of 10, 20, 30, and 40 μm. Figure 3 shows AFM micrographs of the hierarchical (micro- and nano-structures) surface produced on the PDMS sample. The depths of the grooves produced by micromachining, determined by AFM, are in the order of 4 μm.

To study the wetting properties of the samples, we measured the contact angle in areas of (3 × 3) mm² of the produced hierarchical structures. Figure 4 shows images of a water droplet on

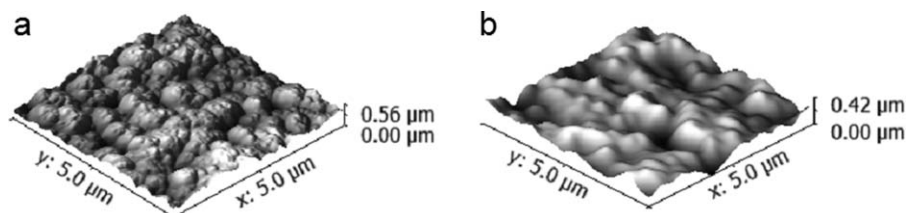


Figure 2. Atomic force micrographs of the ZnO nanowire film (a) and the PDMS stamped sample (b).

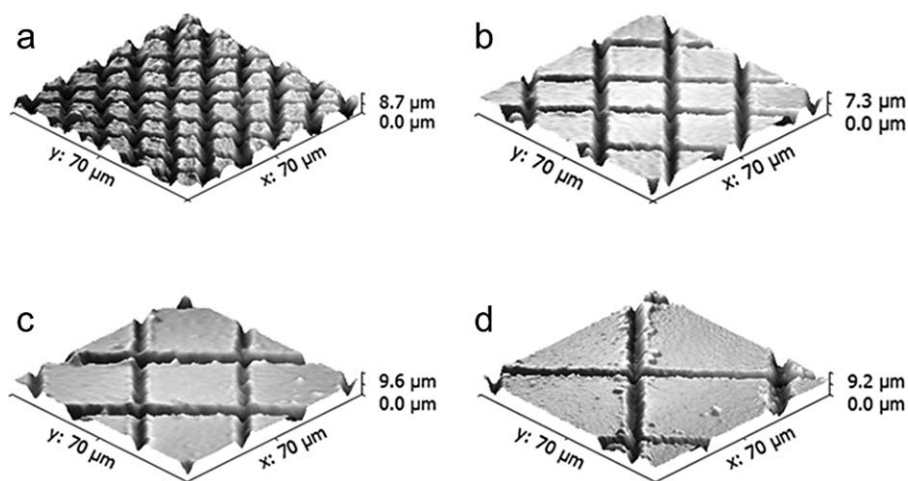


Figure 3. AFM images of nano/microstructured PDMS films with periodicities of 10 μm (a), 20 μm (b), 30 μm (c), and 40 μm (d).

an unstructured (flat) PDMS surface (a) and on a structured surface (20 μm). An increase of 49° was observed in the contact angle for the hierarchical structured surface; the contact angle changed from 121° on the flat surface to 170° in the structured one. The contact angle hysteresis (CAH) was measured by withdrawing liquid from a droplet on the micromachined sample surface (receding contact angle). Similarly advancing contact angle was measured by adding liquid to the droplet. The difference between advancing and receding contact angles is 3° .

Figure 5 shows the contact angle dependence on the periodicity of surface microstructuring (Λ). The data at $\Lambda = 0 \mu\text{m}$ (light gray circle) corresponds to the flat PDMS surface that presents a contact angle of 121° . Upon nanostructuring the PDMS surface by stamping, a contact angle increase of 10° was observed (dark gray circle). The solid circles in Figure 5 show the results obtained for the hierarchically structured surface (nano/micro), for different Λ . As it can be seen, the effect of the hierarchical structuring increases the contact angle by about 49° . In fact, the contact angle obtained for a periodicity of 10 μm is 157° , while for $\Lambda = 20 \mu\text{m}$ a contact angle of approximately 170° was obtained. The open circles in Figure 5 present the contact angle results for samples that were only microstructured (without the nanostructuring produced by stamping). These results show that for $\Lambda = 10 \mu\text{m}$, the hierarchical (solid circles) and only microstructured (open circles) surfaces present the same wetting

properties. For higher periodicities, however, the hierarchical structure (solid circles) exhibits an increase of approximately 15° when compared to the sample that was only microstructured (open circles). This result also indicates that for the hierarchical surface (micro plus nano) the contact angle does not change much with the microstructuring period (Λ), in the range from 10 up to 50 μm .

A decrease of the contact angle with the periodicity is observed in Figure 5 (open circles) for the sample that was only microstructured. According to the Cassie–Baxter model,^{28,29} the liquid in a rough surface does not completely wet it, because air is trapped in the surface gaps (three-phase contact). In this case, small contact angles are observed when the contact area between the solid and the liquid is increased, which in our case occurs when the periodicity of the microstructures in the surface is increased.³⁰ Basically, as the period of the microstructures is increased, the ratio between the water/surface contact area and the projected area approaches one, the value expected for a flat surface. This effect, the decrease of CA with period, does not seem to occur with the hierarchical structure, in which the CA remains constant, within the experimental errors, for all microstructure periods tested. This result indicates that the nanostructuring decreases the water/surface contact area, in such a way to compensate for the effect of augmentation of the period of the nanostructuring.

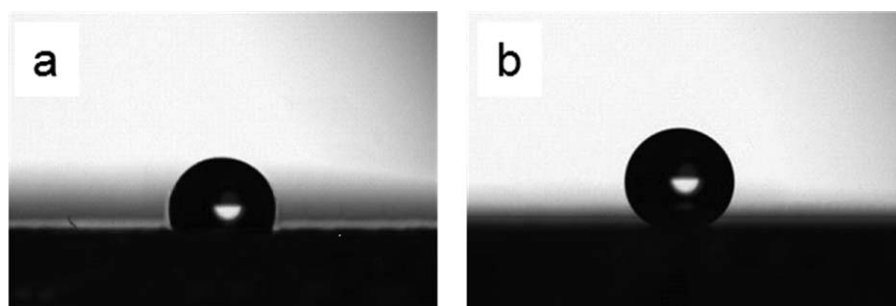


Figure 4. Pictures of a water droplet on a flat (a) and hierarchical (b) structured surface. For the last one, the periodicity of the microstructure is 20 μm .

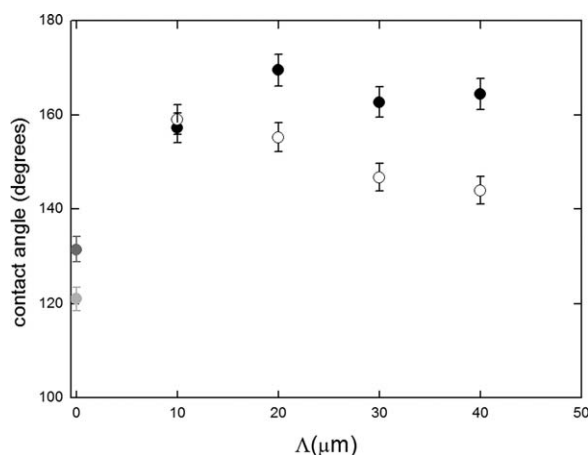


Figure 5. Dependence of contact angle with the microstructuring periodicity for the hierarchical structured surface (nano/micro) (●) and the surface only microstructured (○). The contact angle for the unstructured sample (●) and for the sample only nanostructured (●) are also displayed.

CONCLUSIONS

We demonstrated the fabrication of a hierarchical surface structure, achieved by stamping and subsequent laser micromachining that exhibits superhydrophobicity. The stamping transfers the nanostructured topography of a ZnO nanowires films to a PDMS sample, while the microstructuring is realized, subsequently, by femtosecond laser micromachining. The hierarchical surface does not strongly depend on the period of the microstructure, fabricated by laser micromachining, in the range of 20–40 μm .

ACKNOWLEDGMENTS

The authors acknowledge FAPESP (2011/12399-0), CNPq, CAPES from Brazil and the Air Force Office of Scientific Research (FA9550-12-1-0028) for financial support and Andre L. S. Romero for technical assistance. T. V. acknowledges financial support from the German Research Foundation (DFG) in the frame of the research unit FOR1616.

REFERENCES

- Furstner, R.; Barthlott, W.; Neinhuis, C.; Walzel, P. *Langmuir* **2005**, *21*, 956.
- Wang, S. D.; Lin, B. J.; Hsieh, C. C.; Lin, C. C. *Appl. Surf. Sci.* **2014**, *307*, 101.
- Zhu, J.; Hsu, C.-M.; Yu, Z.; Fan, S.; Cui, Y. *Nano Lett.* **2010**, *10*, 1979.
- Cardoso, M. R.; Tribuzi, V.; Balogh, D. T.; Misoguti, L.; Mendonca, C. R. *J. Optoelectr. Adv. Mater.* **2010**, *12*, 745.
- Baldacchini, T.; Carey, J. E.; Zhou, M.; Mazur, E. *Langmuir* **2006**, *22*, 4917.
- Blossey, R. *Nat. Mater.* **2003**, *2*, 301.
- Neinhuis, C.; Barthlott, W. *Ann. Bot.* **79**, 667.
- Tuteja, A.; Choi, W.; Ma, M. L.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* **2007**, *318*, 1618.
- Yan, Y. Y.; Gao, N.; Barthlott, W. *Adv. Colloid Interface Sci.* **2011**, *169*, 80.
- Sun, T.; Feng, L.; Gao, X.; Jiang, L. *Acc. Chem. Res.* **2006**, *39*, 487.
- Chen, F.; Zhang, D.; Yang, Q.; Yong, J.; Du, G.; Si, J.; Yun, F.; Hou, X. *ACS Appl. Mater. Interfaces* **2013**, *5*, 6777.
- Oner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777.
- Wu, W.; Zhu, Q.; Qing, F.; Han, C. C. *Langmuir* **2009**, *25*, 17.
- Barberoglou, M.; Zorba, V.; Stratakis, E.; Spanakis, E.; Tzanetakakis, P.; Anastasiadis, S. H.; Fotakis, C. *Appl. Surf. Sci.* **2009**, *255*, 5425.
- Otten, A.; Herminghaus, S. *Langmuir* **2004**, *20*, 2405.
- Vogelaar, L.; Lammertink, R. G. H.; Wessling, M. *Langmuir* **2006**, *22*, 3125.
- Patankar, N. A. *Langmuir* **2004**, *20*, 8209.
- Jin, M. H.; Feng, X. J.; Xi, J. M.; Zhai, J.; Cho, K. W.; Feng, L.; Jiang, L. *Macromol. Rapid Commun.* **2005**, *26*, 1805.
- Cortese, B.; D'Amone, S.; Manca, M.; Viola, I.; Cingolani, R.; Gigli, G. *Langmuir* **2008**, *24*, 2712.
- Feng, L.; Li, S. H.; Li, Y. S.; Li, H. J.; Zhang, L. J.; Zhai, J.; Song, Y. L.; Liu, B. Q.; Jiang, L.; Zhu, D. B. *Adv. Mater.* **2002**, *14*, 1857.
- Yang, Y.-L.; Hsu, C.-C.; Chang, T.-L.; Kuo, L.-S.; Chen, P.-H. *Appl. Surf. Sci.* **2010**, *256*, 3683.
- Wu, B.; Zhou, M.; Li, J.; Ye, X.; Li, G.; Cai, L. *Appl. Surf. Sci.* **2009**, *256*, 61.
- Tserepi, A.; Gogolides, E.; Tsougeni, K.; Constantoudis, V.; Valamontes, E. S. *J. Appl. Phys.* **2005**, *98*, 113502.
- McDonald, J. C.; Whitesides, G. M. *Acc. Chem. Res.* **2002**, *35*, 491.
- Bolognesi, A.; Botta, C.; Yunus, S. *Thin Solid Films* **2005**, *492*, 307.
- Shin, Y. S.; Cho, K.; Lim, S. H.; Chung, S.; Park, S. J.; Chung, C.; Han, D. C.; Chang, J. K. *J. Micromech. Microeng.* **2003**, *13*, 768.
- Hou, D.; Dev, A.; Frank, K.; Rosenauer, A.; Voss, T. *J. Phys. Chem. C* **2012**, *116*, 19604.
- Cassie, A. B. D.; Baxter, S. *Trans. Farad. Soc.* **1944**, *40*, 0546.
- Patankar, N. A. *Langmuir* **2003**, *19*, 1249.
- Cardoso, M. R.; Tribuzi, V.; Balogh, D. T.; Misoguti, L.; Mendonca, C. R. *Appl. Surf. Sci.* **2011**, *257*, 3281.