

# Wetting behaviours of a-C:H:Si:O film coated nano-scale dual rough surface

Tae-Young Kim <sup>a,c</sup>, Bialuch Ingmar <sup>b</sup>, Klaus Bewilogua <sup>b</sup>, Kyu Hwan Oh <sup>c</sup>,  
Kwang-Ryeol Lee <sup>a,\*</sup>

<sup>a</sup> Future Technology Research Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 136-791, Republic of Korea

<sup>b</sup> Fraunhofer Institute for Surface Engineering and Thin Films, Bienroder Weg 54 E D-38108, Braunschweig, Germany

<sup>c</sup> School of Materials Science and Engineering, Seoul National University, Kwanak-ku, Seoul 151-742, Republic of Korea

Received 7 August 2006; in final form 10 January 2007

Available online 17 January 2007

---

## Abstract

By combining nano-scale surface roughening with a hydrophobic a-C:H:Si:O coating, we generated the super-hydrophobic surface with very low wetting angle hysteresis. We focused on the effect of the dual structure of the surface on the static and the dynamic wetting behaviours. It was observed that the dual rough surface is super-hydrophobic with a wetting angle around 160° and a wetting angle hysteresis (difference between forwarding and receding angle) less than 5°. On the other hand, mono rough surfaces in any scale appeared sticky and the wetting angle hysteresis ranged from 30° to 60° depending on the dimension of the surface roughness.

© 2007 Elsevier B.V. All rights reserved.

---

## 1. Introduction

Solid surface wettability can be controlled by chemical treatment of the surface and manipulation of the surface topology. Water contact angle can reach 100°–120° by chemical treatment of smooth surfaces. The contact angle further increases up to 150°–170° by introducing surface roughness, which is called super-hydrophobic surface [1–15]. The super-hydrophobic surface has drawn much attention owing to its potential applications such as water repellent self cleaning surface, surface energy induced drop motion or flow channel of low resistance for microfluidics devices [16–18]. Since the water flow over the surface is involved in most applications, both static wetting angle and the wetting angle hysteresis defined by the difference between advancing and receding wetting angle are relevant.

Two models were suggested to explain the increase in wetting angle on the rough surface. Wenzel [19] assumed that the area below water droplet is fully wetted (wetted

surface regime). Therefore, the rough surface increases the contact area between solid and liquid resulting in larger apparent wetting angle. On the other hand, Cassie and Baxter [20] assumed that air can remain trapped below the water droplet (composite surface regime). The composite surface also leads to the increase in wetting angle because a part of water drop sits on air. Wetting angle hysteresis has also been discussed based on these thermodynamic models. Lafuma and Quéré [21] showed that wetting angle hysteresis of wetted surface is larger than that of composite surface due to the liquid pinning effect. McHale et al. [22] theoretically predicted that the wetted surface is sticky whereas the composite surface is slippery. The previous works suggest minimizing the contact area between the solid and liquid in order to obtain a super-hydrophobic surface with low wetting angle hysteresis.

Recently, many researchers focused on the dual rough surface which mimics the lotus leaf to obtain the artificial self cleaning surface. It was theoretically suggested that the dual rough surface is more hydrophobic than mono rough surface, even if the wetting angle hysteresis was not sufficiently addressed [16]. It was experimentally

\* Corresponding author. Fax: +82 2 958 5509.

E-mail address: [klee@kist.re.kr](mailto:klee@kist.re.kr) (K.-R. Lee).

observed that the super-hydrophobicity with a small wetting angle hysteresis appears on the dual rough surface prepared by various methods [23–25]. However, some mono rough surface with an appropriate surface treatment also exhibited the similar slippery surface [26,27]. Therefore, it is not evident yet that the super-hydrophobic slippery surface is originated only from the surface roughness in dual scale.

In the present work, by combining nanoscale surface roughening with a hydrophobic a-C:H:Si:O coating, we investigated the water wetting behaviour of various surface structures. We prepared the mono rough surface of Si using r.f. glow discharge of CF<sub>4</sub> or mixture of CF<sub>4</sub> and O<sub>2</sub> gases. Dual rough structure surface which mimics the lotus leaf was prepared by using nano-sized metal dots as mask of the plasma etching process. Hydrophobic a-C:H:Si:O film was deposited on the nano-structured surface using mixtures of hexamethyldisiloxane (HMDSO) and Ar. Super-hydrophobicity of the wetting angle 160° with the wetting angle hysteresis (difference between forwarding and receding angle) less than 5° appeared only on the dual rough surface. Mono rough surfaces had a high wetting angle around 120° but with relatively high wetting angle hysteresis ranging from 40° to 60°.

## 2. Experimental

Surface of Si (110) wafer was etched by 13.56 MHz r.f. glow discharge of CF<sub>4</sub> or mixtures of CF<sub>4</sub> and O<sub>2</sub> gases (gas flow ratio CF<sub>4</sub>:O<sub>2</sub> = 7:2). The wafer was placed on the cathode where r.f. power was delivered via matching network. The working pressure in the reactor ranged from 2 to 5 Pa and r.f. power from 150 to 300 W. Etched surface was observed using a scanning electron microscope (SEM). In order to prepare dual structured surface, thin Cu films were deposited on Si (110) wafers by DC magnetron sputtering. Rapid thermal annealing of the specimen at 550 °C for 15 min in pure hydrogen environment converted the Cu film into nano-sized dots. Size and distribution of the nano-size dots are dependent on the film thickness [28]. The Cu nano-size dots play a role of mask during CF<sub>4</sub> plasma etching of Si, resulting in dual structure of coarse posts and nano-size fine posts.

We deposited a-C:H:Si:O films on the specimens of various surface structures. The films were deposited by 13.56 MHz r.f. plasma decomposition of mixed gas of HMDSO (hexamethyldisiloxane) and Ar. The surface properties of a-C:H:Si:O film are dependent on the r.f. power and Ar fraction in the precursor gas. More details on deposition process and properties of a-C:H:Si:O films were published earlier [29]. In the present work, we used a hydrophobic a-C:H:Si:O film of static wetting angle 101.8°. Ar fraction in the precursor gas was fixed at 28.6% and r.f. power at 30 W. The films of about 10 nm thickness were deposited at a pressure of 5 Pa. The contact angle measurement was carried out by a goniometer (Data Physics instrument GmbH, OCA 20L) which takes and ana-

lyzes the image of a sessile droplet on the surface. The static wetting angle was measured by gentle landing of 5 µl water drop on the surface. To measure the dynamic wetting angle, the drop volume was continually varied by an automatic dispensing syringe. Advancing angle was measured as the water volume increased from 2 to 5 µl at 0.053 µl/s. Receding contact angle measurement was conducted by removing water from the droplet at the same rate.

## 3. Results and discussion

Fig. 1 shows the surface microstructures prepared in the present work. When using mixture of CF<sub>4</sub> and O<sub>2</sub> gases during plasma etching at the pressure 2 Pa, the etched surface is quite smooth as shown in Fig. 1a. Increasing the pressure to 5 Pa slightly induced the surface undulations. On the other hand, plasma etching with pure CF<sub>4</sub> gas resulted in the etched surface composed of nanometer scale fine posts, also referred to as nano-post, for both etching pressures 2 and 5 Pa. Fig. 1b shows the surface with the nano-posts prepared by CF<sub>4</sub> plasma etching at 5 Pa. Height of the post was measured to be 90.1 ± 11.3 nm and diameter 71.5 ± 10.4 nm. Top solid fraction was estimated to be around 74.2 ± 8.0%. Number density and diameter of the nano-post slightly decreased as the etching pressure decreased to 2 Pa. The observed evolution of the surface structure during CF<sub>4</sub> plasma etching is presumably due to the local deposition of carbon films that would suppress the etching of Si. Oxygen addition will accelerate the etching of the carbon film, resulting in less apparent surface structure evolution. The evolution of the surface structure is essentially the same when the r.f. power increased from 150 to 300 W.

Fig. 1c,d show the morphologies of the surface etched with Cu nano-dots as the mask. Etching behaviours of Si surface are the same as those without Cu nano-dots shown in Fig. 1a,b. When etching with glow discharge of CF<sub>4</sub> and O<sub>2</sub> gas mixture, only coarse posts are found on the smooth Si surface (see Fig. 1c). Cu nano-dots remained on top of the coarse post. Average height of the post was 352.0 ± 53.2 nm and the diameter 360.5 ± 63.1 nm. Top solid fraction of the coarse post, 17.1 ± 5.9%, was much smaller than that of nano-posts. CF<sub>4</sub> plasma etching with Cu nano-dots as the mask, dual rough surface structure was obtained as shown in Fig. 1d, where coarse posts are formed on the nano-posts. Hydrophobic surface coating on this dual rough surface would mimic the lotus leaf that can be characterized by papillose surface with additional layer of epicuticular waxes (see Fig. 1e of Ref. [30]).

Water drops on the four characteristic surfaces with a-C:H:Si:O surface layer are shown in Fig. 2. Fig. 2a is the water drop on the a-C:H:Si:O coated smooth Si surface obtained by etching of Si at the pressure 2 Pa using mixture of O<sub>2</sub> and CF<sub>4</sub>. On the smooth surface, static wetting angle is 101.8° that represent the chemical effect of the a-C:H:Si:O coating. Hysteresis of the wetting angle obtained by dynamic wetting angle measurement was 12.6°. Fig. 2b is

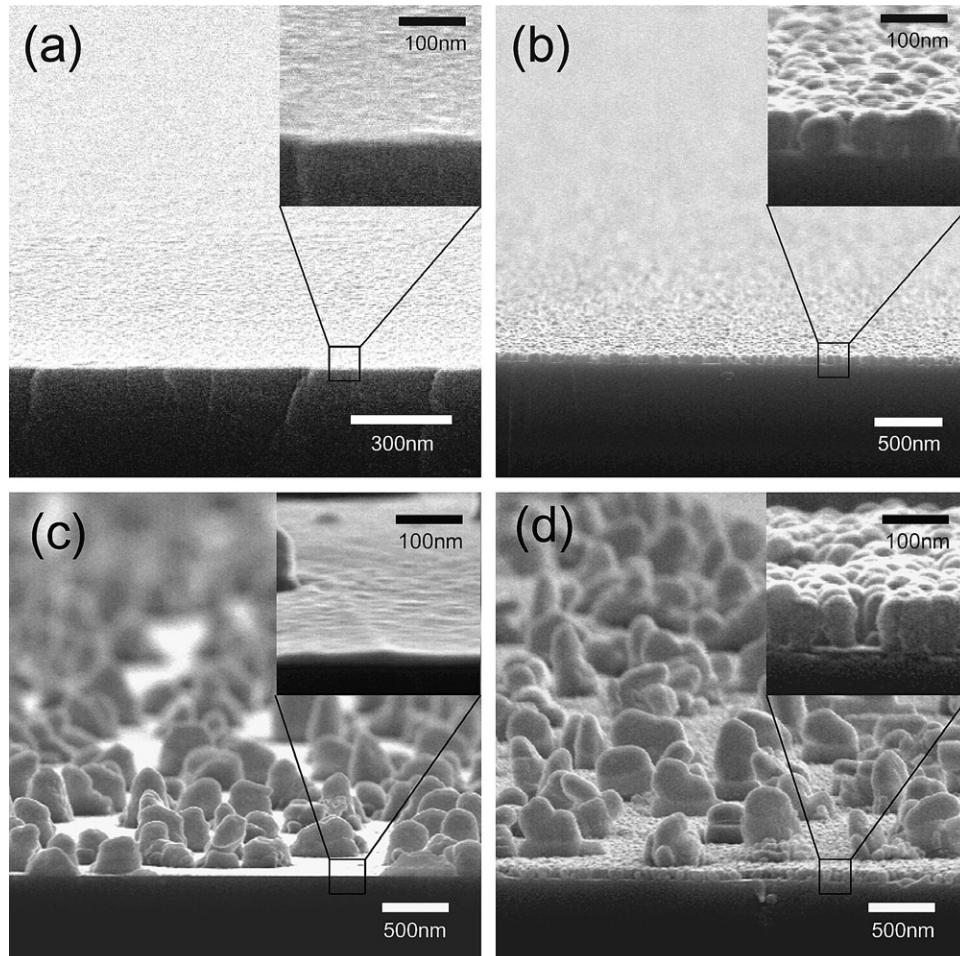


Fig. 1. SEM microstructures of Si surfaces etched at 150 W r.f. power using (a) mixture gas of  $\text{CF}_4$  and  $\text{O}_2$  at 2 Pa, (b)  $\text{CF}_4$  gas at 5 Pa, (c) mixture gas of  $\text{CF}_4$  and  $\text{O}_2$  at 2 Pa with Cu nanodots on the surface, and (d)  $\text{CF}_4$  gas at 5 Pa with the Cu nanodots.

the water drop on the surface of nano-posts prepared by plasma etching with  $\text{CF}_4$  glow discharge as shown Fig. 1b. Nanometer scale surface protrusion considerably increased the wetting angle to  $137.8^\circ$ . Cassie and Baxter angle for composite surface regime and Wenzel angle for wetted surface regime were estimated using the geometry of the nano-post [19,20]. The estimated wetting angles are  $112.7^\circ$  and  $145.4^\circ$ , respectively. The measured wetting angle seems to show that the wetting on the surface with nano-posts does not belong to any two extreme surface regimes. The wetting angle was not significantly dependent on the dimension of the posts. Fig. 2c shows the water drop on the surface of coarse posts shown in Fig. 1c. The wetting angle was  $137.5^\circ$ . These values are also in the middle of the estimated Cassie and Baxter angle ( $149.2^\circ$ ) for composite surface regime and Wenzel angle ( $107.0^\circ$ ) for wetted surface regime. It can be generally said that the wetting angle of the mono rough surface is higher than that of the smooth surface. However, the wetting angle hysteresis on the mono rough surfaces was significant:  $36.7^\circ$  for the surface with nano-posts and  $61.4^\circ$  for the one with coarse posts. This sticky behaviour implies that the wetting might occur inside of the posts of the specimens even when the

spacing between the posts is in nanometer scale [21]. It must be noted that the measured wetting angles on both mono rough surfaces do not belong to any two extreme cases. Partial wetting can be deduced from these results, although the details of the wetting behaviour should be further characterized in both experimental and theoretical methods.

Super-hydrophobicity with small hysteresis was observed only on dual rough surface shown in Fig. 1d. Fig. 2d shows the water drop on the dual rough surface. Wetting angle was  $160.1^\circ$ . The wetting angle hysteresis estimated by a dynamic wetting angle measurement was as small as  $4.3^\circ$ . It is surprising that the super-hydrophobic and slippery surface can be obtained by combining two surface structures of Fig. 1b,c, which is proved to be sticky. Gao and McCarthy [23] reported that the nano-scale roughness on top of the large post is essential for the ‘lotus effect’. However, in the present work where the top surface of the large post is smooth, the dual rough surface is super-hydrophobic and slippery. Morphology of the large post itself seems to play a role in wetting behaviour (top of the Gao’s post is the square and flat [23], while the present posts has a round top surface.). In order to investigate the

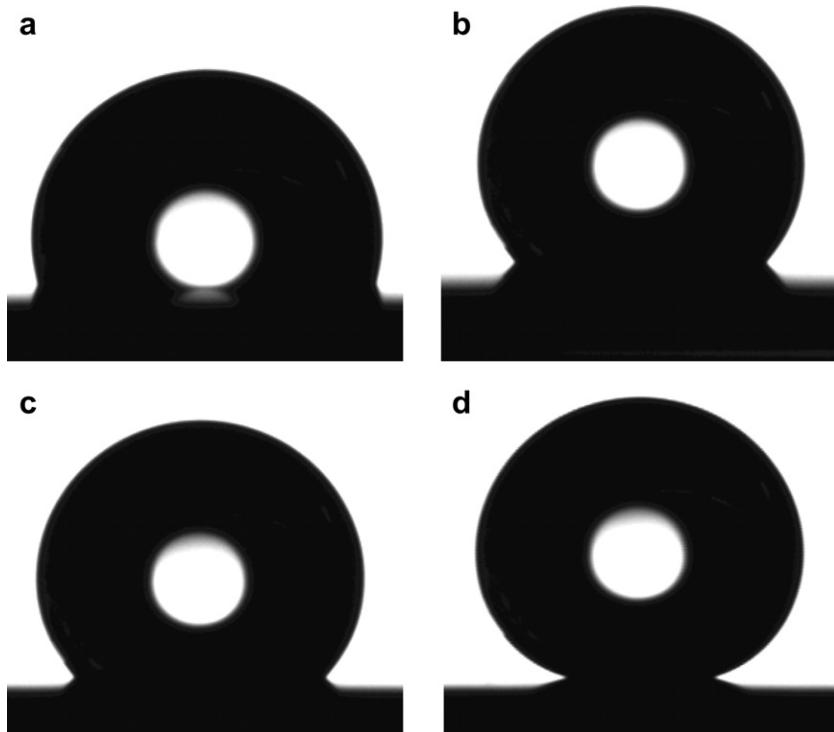


Fig. 2. Photographs of water droplet on the a-C:H:Si:O deposited surface with structure of (a) flat etched surface shown in Fig. 1a, (b) nano-post structure surface shown in Fig. 1b,c coarse post structure surface shown in Fig. 1c,d dual structure surface as shown in Fig. 1d.

role of the coarse posts, wetting angle of the surface of larger number density of the coarse post (see Fig. 3) was also measured. The wetting angle was  $143.4^\circ$  with hysteresis  $33.1^\circ$ . On the other hand, if the number density of the coarse post decreased, the surface became sticky with wetting angle  $125.8^\circ$  and hysteresis  $36.7^\circ$ . This result shows that the super-hydrophobicity with low wetting angle hysteresis occurs at an optimum number density of the coarse posts.

It is generally accepted that the wetted surface is sticky while the composite surface is slippery [21,22]. The present results thus show that on the dual rough surface, the coarse posts with optimum size and distribution effectively suppress the wetting on the bottom surface with nano-posts.

Fig. 4 shows the schematic of the wetting behaviour of the dual rough surface with an optimized spacing of the coarse post. Because of hydrophobic coating on the surface, the shape of the water partially wetting the coarse posts would be convex to the bottom surface. Hence, the interfacial force is directed to the center of water drop, which can suppress the water drop from wetting the bottom surface even when the water drop was forced to approach the bottom surface under a certain dynamic condition. If the spacing between the coarse posts is very large, the water will contact the bottom nano-post with the same geometry of water drop on mono rough surface. On the other hand, if the spacing of the coarse post is too narrow, the water drop will contact only the coarse post of high

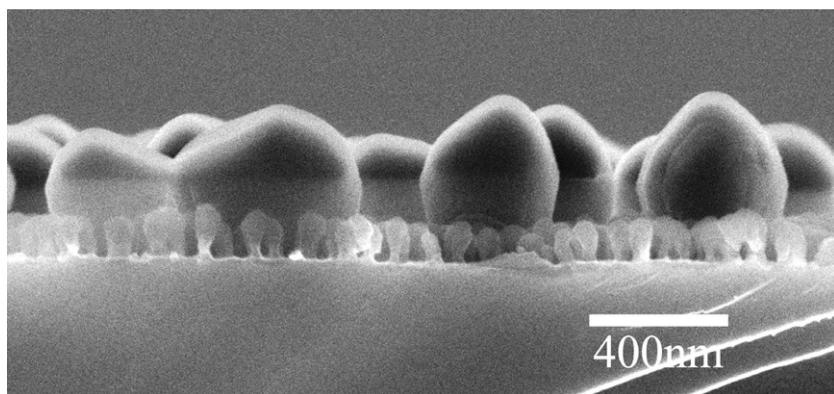


Fig. 3. SEM microstructure of dual structure with higher number density of coarse post than that of dual structure shown in Fig. 1d.

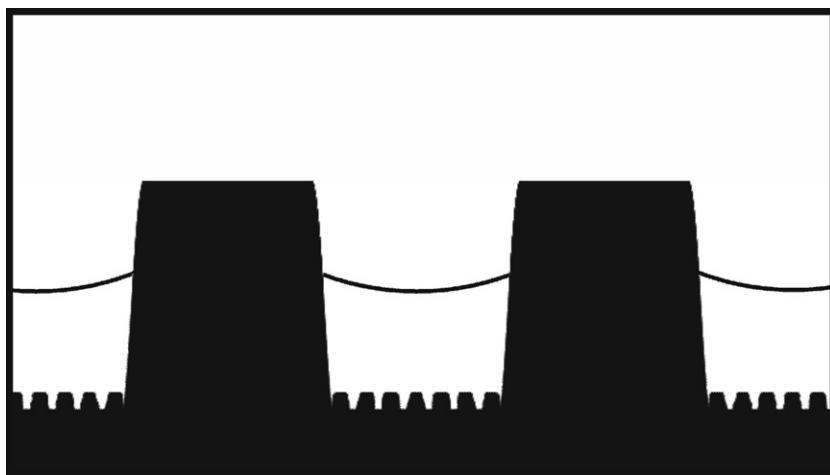


Fig. 4. Schematics of the wetting behaviour on dual rough surface.

solid fraction, which is equivalent to the wetting on the undulated surface. It would be thus important to control the distribution of the coarse post of dual rough surface to obtain the super-hydrophobic and slippery surface.

#### 4. Conclusions

The most significant result of the present work is to show that the super-hydrophobic slippery surface can be obtained by combining two rough surfaces of different scale that are hydrophobic but sticky. The dual rough surface composed of coarse posts on nano-posts with hydrophobic surface layer is super-hydrophobic (wetting angle about 160°) and slippery (wetting angle hysteresis less than 5°). We could manipulate the Si surface structure by employing r.f. plasma etching with metal nano-size dots as the etching mask. This surface structure mimics the dual surface structure of lotus leaf, a natural super-hydrophobic surface. The present results would provide valuable information for the theoretical analysis of the ‘lotus effect’ and address an effective surface structure design for various moving droplet applications.

#### Acknowledgements

This research was supported by a grant (code #: 05K1501-01610) from ‘Center for Nanostructured Materials Technology’ under ‘21st Century Frontier R&D Programs’ of the Ministry of Science and Technology, Korea. Furthermore the research was partly supported by the German BMBF in the frame of a German–Korean joint project (Grant No. 03X2502).

#### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2007.01.036.

#### References

- [1] H. Nakae, R. Inui, Y. Hirata, H. Saito, *Acta Mater.* 7 (1998) 2313.
- [2] J. Bico, C. Marzolin, D. Quéré, *Europhys. Lett.* 47 (1999) 220.
- [3] A. Nakajima, A. Fujishima, N. Hashimoto, T. Watanabe, *Adv. Mater.* 11 (1999) 1365.
- [4] G. Wolansky, A. Marmur, *Colloid. Surf. A* 156 (1999) 381.
- [5] D. Öner, T.J. McCarthy, *Langmuir* 16 (2000) 7777.
- [6] Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. Hashimoto, *Langmuir* 18 (2002) 5818.
- [7] D. Quéré, *Physica A* 313 (2002) 32.
- [8] B. He, J. Lee, N.A. Patankar, *Colloid. Surf. A* 248 (2004) 101.
- [9] J.-Y. Shiu, C.-W. Kuo, P. Chen, C.-Y. Mou, *Chem. Mater.* 16 (2004) 561.
- [10] A. Marmur, *Langmuir* 20 (2004) 3517.
- [11] Y.-H. Cheng, C.-K. Chou, C. Chen, S.-Y. Cheng, *Chem. Phys. Lett.* 397 (2004) 17.
- [12] C.-T. Hsieh, J.-M. Chen, R.-R. Kuo, T.-S. Lin, C.-F. Wu, *Appl. Surf. Sci.* 240 (2005) 318.
- [13] R. Fürstner, W. Barthlott, *Langmuir* 21 (2005) 956.
- [14] N.J. Shirtcliffe, G. McHale, M.I. Newton, C.C. Perry, *Langmuir* 21 (2005) 937.
- [15] J. Zhang, L. Xue, Y. Han, *Langmuir* 21 (2005) 5.
- [16] N.A. Patankar, *Langmuir* 20 (2004) 8209.
- [17] N.A. Patankar, *Langmuir* 19 (2003) 1249.
- [18] C. Cottin-Bizonne, J.-L. Barrat, L. Bocquet, E. Charlaix, *Nat. Mater.* 2 (2003) 237.
- [19] R.N. Wenzel, *Ind. Eng. Chem.* 28 (1936) 988.
- [20] A.B.D. Cassie, S. Baxter, *S. Trans, Faraday Soc.* 40 (1944) 546.
- [21] A. Lafuma, D. Quéré, *Nat. Mater.* 2 (2003) 457.
- [22] G. McHale, N.J. Shirtcliffe, M.I. Newton, *Langmuir* 20 (2004) 10146.
- [23] L. Gao, T.J. McCarthy, *Langmuir* 22 (2006) 2966.
- [24] W. Ming, D. Wu, R. van Benthem, G. de With, *Nano Lett.* 5 (2005) 2298.
- [25] L. Zhu, Y. Xiu, J. Xu, P.A. Tamirisa, D.W. Hess, C.-P. Wong, *Langmuir* 21 (2005) 11208.
- [26] K.K.S. Lau, J. Bico, K.B.K. Teo, M. Chhowalla, G.A.J. Amaratunga, W.I. Milne, G.H. McKinley, K.K. Gleason, *Nano Lett.* 3 (2003) 1701.
- [27] W. Lee, M.-K. Jin, W.-C. Yoo, J.-K. Lee, *Langmuir* 20 (2004) 7665.
- [28] C.S. Lee, T.-Y. Kim, K.-R. Lee, J.-P. Ahn, K.H. Yoon, *Chem. Phys. Lett.* 280 (2003) 774.
- [29] M. Grischke, A. Hieke, F. Morgenweck, H. Dimigen, *Diam. Relat. Mater.* 7 (1998) 454.
- [30] W. Barthlott, C. Neinhuis, *Planta* 202 (1997) 1.