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Making silicon hydrophobic: wettability control by two-lengthscale simultaneous patterning with femtosecond laser irradiation

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Abstract
We report on the wettability properties of silicon surfaces, simultaneously structured on the micrometre-scale and the nanometre-scale by femtosecond (fs) laser irradiation to render silicon hydrophobic. By varying the laser fluence, it was possible to control the wetting properties of a silicon surface through a systematic and reproducible variation of the surface roughness. In particular, the silicon–water contact angle could be increased from 66° to more than 130°. Such behaviour is described by incomplete liquid penetration within the silicon features, still leaving partially trapped air inside. We also show how controllable design and tailoring of the surface microstructures by wettability gradients can drive the motion of the drop's centre of mass towards a desired direction (even upwards).

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1. Introduction

The control of the wettability properties of surfaces, and particularly the possibility of inducing superhydrophilic and superhydrophobic behaviour (the so-called 'Lotus effect' [1]) by micro-nanostructuring is giving rise to increasing interest for a wide range of applications, such as self-cleaning surfaces, biological scaffolds, microfluidics, lab-on-chip devices, coatings for automotive and aerospace vehicles, and textiles [2–4]. Hence, several different physical and chemical patterning approaches have been employed for structuring surfaces, thus tailoring their wettability, including photolithography [5–8], templated electrochemical deposition [9], plasma treatments [10–12], electron-beam lithography [13], and selective growth of carbon nanotubes [14, 15]. The effect of superhydrophobicity is also widespread in nature and can be found in many plants (*Nelumbo Nucifera*, *Alocasia Macrorrhiza*, *Rosa Landora* etc) and insects such as *Lepidoptera* [16] and *Rhinotermitidae* [17] to ensure water repellency.

It has been demonstrated that the degree of hydrophobicity of a surface can be greatly enhanced by structuring the surfaces that are used at two different lengthscales (micrometre-scale and nanometre-scale) [18–20]. To date, there are few works that report the realization of these two-scale surface topologies by the use of complex, multistep patterning procedures [19]. Simplified schemes of micro-nanomanufacturing, enabling the reproducible creation of complex surface topologies with two lengthscales, are therefore very desirable. Among possible patterning methods, microstructuring of silicon by femtosecond (fs) and nanosecond (ns) lasers [21–23] is particularly attractive, because of the peculiar morphological and electronic properties exhibited by the processed surfaces. In particular, quasi-ordered arrays of cone-shaped micro-tips (i.e. spikes) covering the irradiated area can be fabricated by employing this method. As has been shown in previous work, fs laser irradiation may induce a disordered roughness on the spikes that are formed, with the appearance of features of sub-micron radius covering the surface [24]. This can be crucial for wettability applications.

In this work, we report on the wettability properties of silicon surfaces, simultaneously structured at the micrometre-scale and the nanometre-scale by fs laser irradiation *to render silicon hydrophobic* without additional steps involving the deposition of hydrophobic coatings. By changing the laser fluence, we affect the topology of silicon and we analyse the impact of this topology on the water contact angle, tuned between 66° and more than 130°, and investigate the wetting behaviour in terms of a partial penetration of the liquid within the recessed two-scale surface roughness. This behaviour can be exploited for inducing spontaneous motion of liquids, since we demonstrate that it is possible to drive drops to ascend a structured silicon surface, tilted at any angle, by properly texturing it with a gradient of wetting surface topologies. By varying parameters other than the laser fluence (e.g. number of laser pulses) contact angles as high as 160° were measured.

2. Experimental details

Single-crystal n-type (phosphorous doped) silicon wafers (100) with a resistivity of $\rho = 2$–$8\ \Omega$ cm are mounted in a vacuum chamber evacuated down to a residual pressure of 10^{-2} mbar by means of a rotary pump. A constant SF_6 pressure of 500 Torr was maintained during the process through a precision micro valve system. The laser system that was employed consisted of a regenerative amplified Ti:sapphire ($\lambda = 800$ nm) delivering 150 fs pulses at a repetition rate of 1 kHz. The sample was positioned on a high-precision X–Y translation stage (computer controlled) normal to the incident laser beam. A mechanical shutter was synchronized to the translation stages, allowing accurate irradiation of the samples. Each sample was fabricated at constant fluence (ranging from 0.17 to 1.8 J cm^{-2}), and the morphology of the corresponding textured silicon surfaces was then characterized by scanning electron microscopy (SEM). An image processing algorithm was implemented in order to obtain quantitative information concerning the macroscopic characteristics of the structures that were formed, i.e. spike density, height, cone tip radius and distribution, from top and side-view SEM pictures of the structured areas. Prior to contact angle measurements, the samples were treated in a 10% HF aqueous solution in order to remove the oxide grown on the surface of the spikes. The static contact angle was determined by the sessile drop method with a contact angle meter using a 2 μl distilled, deionized Millipore water (18.2 MΩ) drop. The Material Interface Associates Inc. automated tensionmeter used to determine the contact angle is based on a collection of digital images of sessile drops. The drop was formed from a capillary tip, and was detached gently from the tip onto the silicon substrate.

Samples with a specific gradient of wettability were obtained by varying the range of fluence (from 0.33 to 1.0 J cm^{-2}) incident on adjacent areas (of size around 1.5 mm), while maintaining a constant average number of pulses (500). The silicon surface with a wettability gradient was placed on a track (0°) and on tilted planes (25° and 90°). A 4 μl distilled water drop was positioned on the highly hydrophobic edge of the gradient and the resulting upward motion of the drop was recorded by a camera that collected 25 frames s^{-1}.

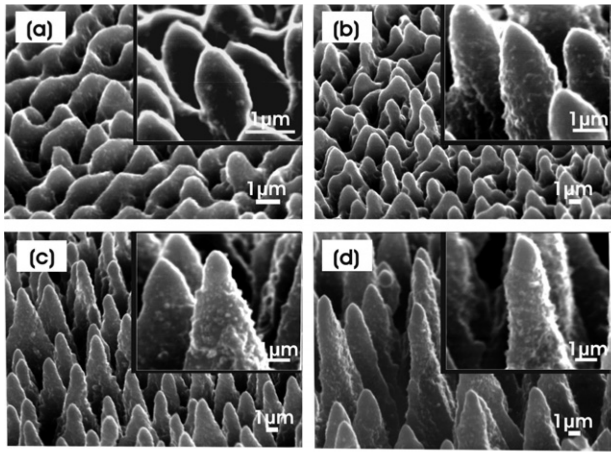

Figure 1. Side scanning electron microscope view of silicon surfaces structured by fs irradiation at different laser fluences: (a) 0.33 J cm^{-2}, (b) 0.56 J cm^{-2}, (c) 0.78 J cm^{-2}, and (d) 1.0 J cm^{-2}. The insets are higher magnifications of the obtained structures.

3. Results and discussion

The textured silicon surfaces realized by employing the same number of laser pulses (an average of 500) at different fluences are displayed in figure 1. Increasing the incident energy per unit area causes remarkable changes in the structure's shape, dimension and density. At low irradiation fluences, laser heating induces melting of the surface, producing a rippled landscape with structures not completely physically separated (figure 1(a)). Upon increasing the fluence (figures 1(b) and (c)), conical microstructuring is promoted on the silicon surface, with structures becoming more pronounced and spatially separated. In this regime, the average spike spacing, base diameter and height increase with laser fluence. For larger fluence values (above ~1.0 J cm^{-2}), the spike's growth reaches a plateau, where the base diameters stabilize around 8 μm, while the height stabilizes around 15 μm.

Besides directly affecting the micrometre-scale surface topology, increasing fluence is also crucial to inducing a more pronounced sub-micrometre decoration on the spikes walls. In particular, the protrusions with sizes from tens to a few hundreds of nanometres, which provide the double lengthscale pattern on the silicon surface, become more evident as the laser fluence increases (insets of figures 1(c) and (d)). The micrometre-scale features generated by the spikes' landscape, together with the nanometre-scale features generated by the surface prongs on the cones, result in a significant increase in the overall roughness. Figure 2 demonstrates the fluence dependence of both the spikes' density on the textured surface and the sessile drop (2 μl) contact angle resulting from the engraved topology. For fluence values ranging from 0.17 to 1.0 J cm^{-2}, the spikes' density decreases fairly linearly, and then saturates at about 10^6 cm^{-2}. Correspondingly, the contact

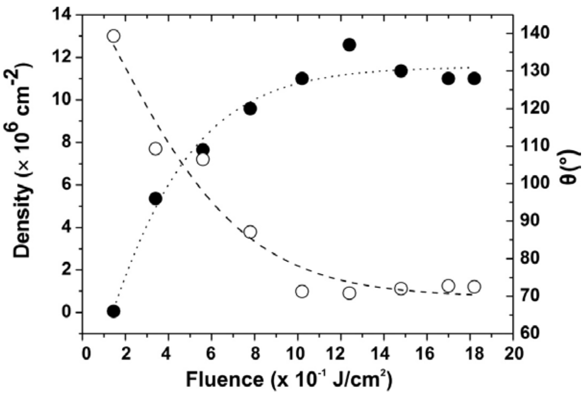

Figure 2. Experimental plot of the spikes' density (empty dots) and the static water contact angle, θ (full dots) on the structured silicon, versus fs laser irradiation fluence. The dotted and the dashed lines are guides for the eye.

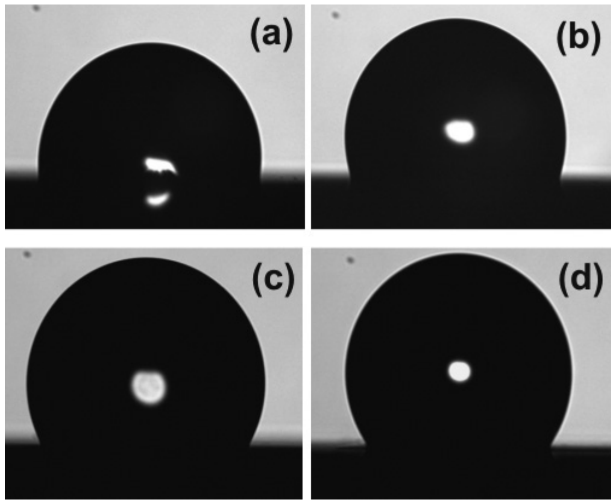

Figure 3. Photographs of water droplets on silicon surfaces structured by fs irradiation at different laser fluences: (a) 0.33 J cm^{-2} (contact angle: 96°), (b) 0.56 J cm^{-2} (contact angle: 109°), (c) 0.78 J cm^{-2} (contact angle: 120°), and (d) 1.0 J cm^{-2} (contact angle: 128°).

angle stabilizes at around 131° for irradiation fluence values greater than 1.0 J cm^{-2}. Some pictures of the water drops lying on the structured silicon surfaces are shown in figure 3. It is evident that the fs laser-assisted texturing of the silicon surface induces a remarkable change in the wettability of silicon, as it affects the overall surface topography in a systematic manner. The contribution of the second-lengthscale roughness on the wetting behaviour will be discussed in detail in future work.

Changes in the observed wettability may be attributed to a synergy of surface chemistry and roughness effects. Chemical analysis of the Si microstructures produced by irradiation with fs laser pulses under similar conditions to those employed in the present work has been reported by Crouch *et al* [25, 26]. Following a detailed study of the structured Si composition and crystallinity, these authors have shown that the fabricated cones consist of a crystalline Si core covered by a disordered S-doped Si layer, a few hundred nanometres thick. For the laser fluences employed, which are similar to those used in the present experiments, the thickness of this disordered layer was found to remain almost unaltered. Also, the dopant (S) concentration did not change significantly and was always less than 1%. Furthermore, it is known that, following treatment by HF, as in the present experiments, the formation of a native silica layer is initiated on the Si surface [27, 28]. This layer is formed immediately after the HF treatment, while its thickness changes very slowly in the first few hours [29] (an increase of ~2 Å in the first hour). Particular care was taken during our experiments to perform the contact angle measurements only a few minutes after the HF treatment, therefore ensuring the presence of similar native oxide thicknesses in all the samples. Based on the above findings, the structured Si surfaces are considered to maintain a similar chemical composition, and any observed changes in the wettability may be attributed primarily to the morphological changes obtained at different laser fluences.

In order to further elucidate the contribution of the overall surface chemical composition on the wetting properties, we made two different sets of contact angle measurements. First, we compared the water contact angles formed on flat crystalline silicon (c-Si) surfaces with different levels of doping, after HF treatment. In the second set of experiments, we compared the contact angles formed on flat heavily P-doped (100 ppm) amorphous silicon (a-Si) samples to that of c-Si, also after HF treatment. In all cases, a similar contact angle of ~70° was measured. These results indicate that the surface composition has a minor contribution to the wetting properties that we observe.

The effect of the macroscopic surface roughness on the wettability has been explained by two different theories. The complete penetration of the liquid drop within the structured surface, described as the 'homogeneous wetting regime', is modelled by the following Wenzel equation [30]:

$$\cos\theta_{\mathrm{w}} = r\cos\theta_{\mathrm{Y}}, \tag{1}$$

where θ_{w} is the Wenzel liquid–solid contact angle, $r > 1$ is the surface ratio, i.e. the overall area of the structured surface projected on the horizontal plane of the solid, and θ_{Y} is the liquid contact angle on the flat surface, otherwise known as the Young contact angle. A description of the wetting behaviour by a pure Wenzel model can be ruled out in our case, since this would predict, for a solid with $\theta_{\mathrm{Y}} < 90°$, a reduction in the contact angle upon structuring.

The case of 'heterogeneous wetting regime', where air is trapped inside the features underneath the liquid drop, is described by the Cassie–Baxter model [31, 32]:

$$\cos\theta_{\mathrm{CB}} = r_f f\cos\theta_{\mathrm{Y}} + f - 1. \tag{2}$$

In the above expression, θ_{CB} is the Cassie–Baxter contact angle, f is the fraction of the projected solid surface that is wetted by the liquid, and r_f is the roughness ratio of the wet area. When the liquid drop is lying on the top of the rough surface without sinking into the features, the factor $r_f = 1$ and equation (2) becomes the widely used simplified form of the Cassie–Baxter equation. In contrast, when $f = 1$ and $r_f = r$, equation (2) turns into the Wenzel equation.

Previous studies, in which initially hydrophilic surfaces became hydrophobic upon structuring, were based on the deposition of a hydrophobic coating on the top of the

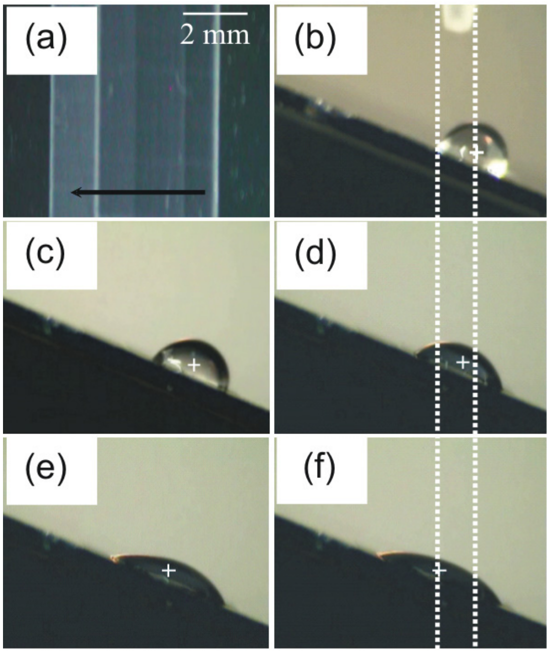

Figure 4. (a) Optical microscope picture of the silicon surface structured with a wettability gradient. The four laser fluences used were 1.1, 0.78, 0.56 and 0.33 J cm^{-2}, respectively. The arrow indicates the direction of increasing hydrophilicity (decreasing laser fluence). Photograph of a water drop ascending the same area tilted at 25°. Time from drop deposition: 0 (b), 2.4 (c), 5.0 (d), 5.8 (e), and 7.6 s (f). The shift of the centre of mass from the initial to the final position is marked by the vertical white-dashed lines.

(This figure is in colour only in the electronic version)

structure [33]. In contrast, the results of this work demonstrate that a silicon surface becomes hydrophobic upon patterning, without any need for coating deposition. The silicon hydrophobicity increases upon patterning, and that this behaviour can be described by assuming that air pockets are trapped beneath the liquid. Equation (2), which describes this behaviour, can give quantitative information about the partial penetration of the water drop into the formed silicon features. For the samples exhibiting the pronounced two-lengthscale surface roughness, namely those obtained by irradiation fluences larger than 1.0 J cm^{-2}, the contact angle values reach a plateau at around 131° (see figure 2). Therefore, for these samples, the liquid is in contact with a practically constant solid surface, and thus the factors f and r_f in equation (2) remain constant. Assuming that, in these irradiation regimes, the structures that are formed roughly resemble cones (the nanometre-scale formed features are integrated into the cone structure), a simple trigonometry equation correlates the factor r_f with the angle of the cones that are formed, which is evaluated using the scanning electron microscopy pictures. Finally, by equation (2), the factor f is calculated to be $\sim$0.13. Namely, the surface of the base of the wetted silicon cone is about 13% of the total base of the silicon cones that are formed (see the supporting information available at stacks.iop.org/Nano/17/3234).

In order to quantify the relative contribution of the second lengthscale structures to the wettability of structured Si, we have treated this type of roughness separately. An estimation of the density of the smaller-scale structures per unit area was made, using high-magnification SEM pictures combined with an image processing algorithm. The second-lengthscale structures, which are observed in high-magnification SEM images (insets of figure 1) and are expected to contribute to the overall roughness, have a radius of the order of $\sim$50 nm. By treating these smaller-scale structures as hemispheres, we have found that the overall roughness ratio of the wetted area increases with laser fluence, reaching up to $\sim$12% in the plateau region, in comparison with the macroscopic cone roughness. By incorporating this value into the Cassie–Baxter equation, we have found a decrease in the fraction of the projected solid surface that is wetted by $\sim$7% (see the supporting information available at stacks.iop.org/Nano/17/3234). This indicates that the second-scale roughness contributes to the overall roughness and, consequently, to the wettability of the Si surface. However, this contribution is small compared to that of the micrometre-scale roughness.

It is known that a gradient in surface tension can induce net motion of a liquid drop on a surface. Such flow, arising from the action of a surface tension gradient, can be created by several approaches, including thermal [34], chemical [35], electrochemical [36] and light-driven methods [37]. The present results pave the way to the possibility of designing and fabricating specific textures on the silicon surface, in order to induce anisotropic wetting and spontaneous motion of liquids, even upwards. To achieve a surface tension gradient on the Si surface, we have structured a series of successive regions with varying laser fluences, which correspond to different morphologies, thus inducing a wettability gradient. A silicon surface structured in this manner is shown in figure 4(a). On this surface, we could observe the centre of mass of a water drop (4 μl) ascending a 25°-tilted silicon surface fabricated by varying the fs irradiation fluence from 0.33 to 1.0 J cm^{-2} (figures 4(b)–(f)). Upon resting the droplet on the area irradiated with the highest fluence (more hydrophobic), it spontaneously moves towards the regions irradiated with lower fluences (less hydrophobic). The advancing edge of the liquid contacts the adjacent area which is more hydrophilic (corresponding to irradiation fluences <0.56 J cm^{-2}) and the drop starts elongating in the direction of the motion, with a corresponding increase in the upward drop speed. The upward velocity of the centre of mass (M) is about 0.10 mm s^{-1} (the time variation of the coordinate, x_M, along the surface is plotted in figure 5). In order to design surfaces with a suitable wettability gradient, aiming to achieve upward motion of liquids on substrates tilted at any angle, α, one can take into account the regime of constant speed [38]: $\dot{x}_M = \upsilon_0 - \upsilon_g$. In this expression, υ_0 is the velocity of the drop on a horizontal plane, and υ_g stands for the gravity contribution disfavouring the upward motion of the liquid ($\upsilon_g \cong Cg \sin\alpha$, where the coefficient C is expressed in time units and g is the acceleration due to gravity). Since, for our silicon surfaces, the measured speed of the drop on the 0° plane is about 0.16 mm s^{-1}, we found that $\dot{x}_M > 0$ even for $\alpha = 90°$. Therefore, the spontaneous upward motion of the liquid is also achievable on completely vertical surfaces. In fact, we could observe water droplets climbing 90°-tilted planes (see the supporting information available

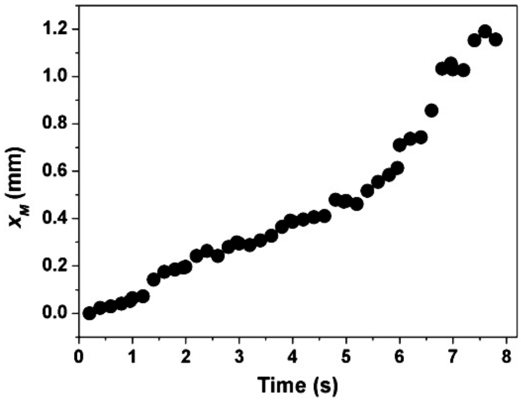

Figure 5. Time dependence of the position of the drop's centre of mass on the structured silicon surface, $x_M(t)$.

at stacks.iop.org/Nano/17/3234). Such effective anisotropic wetting and spontaneous motion of liquids can be very useful for self-cleaning surfaces and microfluidic applications.

4. Conclusion

In conclusion, we have demonstrated that fs laser irradiation may be employed to render silicon hydrophobic without any additional surface coating. The resulting structures consist of both conical spikes with a characteristic size between a few microns and a few tens of microns, and fine features between tens of nanometres and a few hundred nanometres. Such simultaneous patterning of the silicon surface at two lengthscales allows one to control the wettability properties. In particular, upon increasing the fs laser fluence from 0.17 to 1.8 J cm^{-2}, we achieved an enhancement of the water contact angle from 66° to greater than 130°. The generalized Cassie–Baxter equation describes the wetting behaviour of our samples by taking into account incomplete liquid penetration. The fs micro-nanomanufacturing of silicon spikes can also be employed for fabricating controlled gradients of wettability, which drive the anisotropic wetting and the spontaneous motion of water droplets, both on horizontal surfaces and on planes tilted at any angle.

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References

[1] Barthlott W and Neinhuis C 1997 *Planta* **202** 1
[2] Nakajima A, Fujishima A, Hashimoto K and Watanabe T 1999 *Adv. Mater.* **11** 1365
[3] Yoshimitsu Z, Nanajima A, Watanabe T and Hashimoto K 2002 *Langmuir* **18** 5818
[4] Patankar N A 2003 *Langmuir* **19** 1249
[5] Öner D and McCarthy T J 2000 *Langmuir* **16** 7777
[6] Shirtcliffe N J, Aqil S, Evans C, McHale G, Newton M I, Perry C C and Roach P 2004 *J. Micromech. Microeng.* **14** 1384
[7] Krupenkin T N, Taylor J A, Schneider T M and Yang S 2004 *Langmuir* **20** 3824
[8] Shiu J-Y, Kuo C-W, Chen P and Mou C-Y 2004 *Chem. Mater.* **16** 561
[9] Bartlett P N, Baumberg J J, Birkin P R, Ghanem M A and Netti M C 2002 *Chem. Mater.* **14** 2199
[10] Woodward I, Schofield W C E, Roucoules V and Badyal J P S 2003 *Langmuir* **19** 3432
[11] Youngblood J P and McCarthy T J 1999 *Macromolecules* **32** 6800
[12] Morra M, Occhiello E and Garbassi F 1989 *Langmuir* **5** 872
[13] Martines E, Seunarine K, Morgan H, Gadegaard N, Wilkinson C D W and Riehle M O 2005 *Nano Lett.* **5** 2097
[14] Lau K K S, Bico J, Teo K B K, Chhowalla M, Amaratunga G A J, Milne W I and Gleason K K 2003 *Nano Lett.* **3** 1701
[15] Huang L, Lau S P, Yang H Y, Leong E S P and Yu S F 2005 *J. Phys. Chem.* B **109** 7746
[16] Bergeron V and Quere D 2001 *Phys. World* **14** 27
[17] Watson G S and Watson J A 2004 *Appl. Surf. Sci.* **235** 139
[18] Patankar N A 2004 *Langmuir* **20** 8209
[19] Zhu L, Xiu Y, Xu J, Tamirisa P A, Hess D W and Wong C P 2005 *Langmuir* **21** 11208
[20] Feng L, Li S, Li Y, Li H, Zhang L, Zhai J, Song Y, Liu B, Jiang L and Zhu D 2002 *Adv. Mater.* **14** 1857
[21] Her T-H, Finlay R J, Wu C, Deliwala S and Mazur E 1998 *Appl. Phys. Lett.* **73** 1673
[22] Zorba V, Alexandrou I, Zergioti I, Manousaki A, Ducati C, Neumeister A, Fotakis C and Amaratunga G A J 2004 *Thin Solid Films* **492** 453
[23] Zorba V, Tzanetakis P, Fotakis C, Spanakis E, Stratakis E, Papazoglou D G and Zergioti I 2006 *Appl. Phys. Lett.* **88** 081103
[24] Crouch C H, Carey J E, Warrender J M, Aziz M J, Mazur E and Génin F Y 2004 *Appl. Phys. Lett.* **84** 1850
[25] Crouch C H, Carey J E, Shen M, Mazur E and Genin F Y 2004 *Appl. Phys.* A **79** 1635
[26] Younkin R, Carey J E, Mazur E, Levinson J A and Friend C M 2003 *J. Appl. Phys.* **93** 2626
[27] Morita M, Ohmi T, Hasegawa E, Kawakami M and Suma K 1989 *Appl. Phys. Lett.* **55** 562
[28] Shimizu H and Munakata C 1990 *Semicond. Sci. Technol.* **5** 842
[29] Morita M, Ohmi T, Hasegawa E, Kawakami M and Ohwada M 1990 *J. Appl. Phys.* **68** 1272
[30] Wenzel R N 1936 *Ind. Eng. Chem.* **28** 988
[31] Cassie A B D and Baxter S 1944 *Trans. Faraday Soc.* **40** 546
[32] Marmur A 2003 *Langmuir* **19** 8343
[33] Shirtcliffe N J, McHale G, Newton M I and Perry C C 2005 *Langmuir* **21** 937
[34] Cazabat A M, Heslot F, Troian S M and Carles P 1990 *Nature* **346** 842
[35] Chaudhury M K and Whitesides M 1992 *Science* **256** 1539
[36] Gallardo B S, Gupta V K, Eagerton F D, Jong L I, Craig V S, Shah R R and Abbott N L 1999 *Science* **283** 57
[37] Ichimura K, Oh S K and Nakagawa M 2000 *Science* **288** 1624
[38] Gary C H Mo, Wei-yang L and Daniel Y K 2005 *Langmuir* **21** 5777