Assessment of roughness and chemical modification in determining the hydrophobic properties of metals†

Iain A. Larmour, Graham C. Saunders and Steven E. J. Bell*

Received (in Montpellier, France) 21st November 2007, Accepted 7th February 2008
First published as an Advance Article on the web 27th February 2008
DOI: 10.1039/b718006c

"Etch and coat" methods, potentially useful for large scale production of superhydrophobic surfaces on metals, have been extended by introduction of a thin 20 nm Au interlayer which allowed thiol surface modifiers to be investigated. Fe, Ti and Zn surfaces modified in this way with a polyfluorothiol generally had lower contact angles, θ, than their silane modified equivalents but were more uniform and reproducible. The higher θ values for silanes appear to be associated with an increased effective roughness that is not seen in the thiol coatings, which follow the underlying surface. For Fe, Ti and Zn, θ increased to a maximum with etching time but then decreased significantly. Electron microscopy of samples etched for long times showed fewer grain boundaries, suggesting that the loss of hydrophobicity was related to reduced roughness. This was confirmed through quantitative measurements of roughness parameters which were directly correlated with the observed contact angles through the Wenzel equation. The observation of this behaviour for 3 different metals suggests it is a general effect and the assumption that increased etch times will give increased roughness is incorrect. Although etching, Au coating and thiol modification did not provide sufficient roughness for superhydrophobicity, electrodeposition of a Cu layer onto the metal substrates followed by electroless deposition of silver gave uniform surfaces with very high contact angles (up to $\theta = 168.9°$) and low roll-off angles ($\alpha < 1°$). This method is sufficiently simple and inexpensive to be suitable for application on industrial scales, for example in marine or aeronautical engineering.

Introduction

Many of the potential applications of superhydrophobic materials will require methods for the production of coatings on industrial scales and in areas such as aeronautical and marine engineering the most useful materials will be those that can be applied to very large (≥ 100 m^2) areas of a metal substrate. Typically artificial superhydrophobic coatings are designed to mimic those observed for natural systems,[1] such as lotus leaves,[2,3] by creating an appropriately rough or textured surface and then adding a low energy surface coating. There are two well known wetting states on rough surfaces: in the Wenzel state the liquid forms a continuous film that covers the surface features while in the Cassie-Baxter state the liquid sits on top of the features but does not penetrate between them. Superhydrophobic surfaces with very high contact angles and low roll off angles are invariably found to be the in Cassie-Baxter state.[4] The majority of superhydrophobic surfaces currently prepared are based on silicon,[5–9] for which manufacturing techniques from the semiconductor industry allow accurate top-down control of surface structure. There are also reports of the use of carbon nanotube forests,[10–12] but it is clear that surfaces of this kind have manufacturing limitations to scale-up.

Several reports have discussed methods to achieve roughness, and consequently superhydrophobicity, on metal surfaces.[13–16] The two main methods of applying sufficient roughness are etching a metal substrate[14] and electroless deposition of a metal coating onto the substrate.[15] The latter gives superb contact angles compared to etching but is confined to metals with appropriate redox potentials. Other methods which produce metal-based superhydrophobic surfaces include sulfur treatment, either with sulfur gas[17] or direct mixing of a thiol solution with a metal (Cd or Zn) salt solution.[18] Electrochemical methods to provide roughness have also been reported for indium tin oxide (ITO)-coated glass[19] and doped silicon.[20] A range of techniques, including anodisation have been successfully applied to Al.[21]

There have been only a few reports that deal with the preparation of a super- or ultra-hydrophobic coating on bulk industrially relevant metals.[13–15,22,23] However, within these reports there are two different approaches to lowering the surface energy of the roughened surfaces: use of fluorinated silanes[14,22] or of fluorinated thiols.[15] Superhydrophobic surfaces based on patterned Si are typically prepared using silane modification to lower the surface energy.[5–7] This is an obvious choice since the underlying chemistry has been thoroughly investigated.[24] For metals the range of compounds that could be used to lower the surface energy is much larger since there

---

Innovative Molecular Materials Group, School of Chemistry and Chemical Engineering, Queen's University Belfast, UK.
E-mail: s.bell@qub.ac.uk; Fax: +44 (0) 9097 6524;
Tel: +44(0) 28 9097 4470

† IAL thanks DEL(NI) for a studentship. We thank Patrick Marks of Hitachi High-Technologies for loan of an instrument and Dr Michael Boyle for assistance in preparing sputtered samples.

are numerous functional groups that bind to metals.[25] Despite this potential diversity, modification of Au and Ag surfaces is almost universally by thiol modification because thiols bind strongly (particularly to Au) and are known to produce a well-ordered close-packed monolayer upon adsorption.[26–29] Adsorption of thiols onto a surface also removes surface contaminants[26] and reverses surface oxidation in the case of silver.[27] Mass equilibrium of an adsorbing thiol has been achieved in approximately one minute and the monolayer can then "mature" in air.[28] This is important for large scale applications since the low surface energy coating can be applied without heating or the extended reaction times that are necessary for silanes. Thiols also provide the opportunity of incorporating functionality onto the surface of the superhydrophobic article.[30]

For the metals which are important for industrial and engineering applications, such as Fe, Zn (galvanized surfaces) and Ti, direct thiol modification of the surfaces is compromised by the chemistry of the metal itself. For these metals, silanes are often used to lower the surface energy of textured or roughened metal substrates. This is a natural extension of work on Si surfaces but as a result published studies on superhydrophobic metal coatings have typically involved Ti, Fe or Zn surfaces treated with silanes and Ag and Au surfaces treated with thiols. There are significant differences between the reported properties of these systems[14,15] and we are interested in finding the origin of these differences. In particular, we would like to improve the hydrophobicity previously achieved for metals, such as Ti and Fe, to the very high levels we have obtained for thiol-modified Au and Ag electrolessly deposited on Cu and Zn substrates.[15]

Despite the diversity of approaches which have been applied to creating superhydrophobic metal surfaces there are just two factors which dominate the ultimate performance. One is the roughness or texture of the surface, the second is the nature of the surface modifying layer. The purpose of this paper is to investigate the interplay between these two factors for industrially important metals, in particular we are interested in finding ways to break the link between the nature of the textured metal and the modifying chemical layer so that each can be investigated separately, *i.e.* one group of modifiers, silane or thiol, to be used on all types of surfaces. It is hoped that this will allow us to both rationalize the diverse data which are available and to establish general guidelines for the preparation of various types of hydrophobic metal surfaces.

Experimental

Wet etching

Copper foil, 99.9%, 15 × 35 mm, 0.25 mm thickness (Advent research materials), was etched in 70% HNO_3 (Riedel-de Haën) for 3–5 seconds. Since etching rates were observed to be different between completely fresh acid and that which had been used previously, the first sample etched in fresh acid was discarded. (*Care should be exercised with this combination*).

The other metal foils used throughout this investigation were: Iron, 99.99+% (Aldrich), Titanium, 99.7% (Aldrich) and Zinc, 99.95+%, (Goodfellow). All foils were 0.25 mm thick and surfaces 15 × 35 mm were cut and used throughout. Etching was carried out as follows. Iron was etched in 37–38% HCl (JT Baker) for 0, 1, 2, 3, 4 and 8 minutes. Titanium was etched in 10% HF (AnalaR, Hopkins and Williams) for 10 and 30 seconds, and 1, 2, 4 and 5 minutes, the upper limit being determined by the time taken for the metal to dissolve completely (6 to 7 minutes). Zinc was etched in 4 M HCl[14] (JT Baker) for 1, 2, 3, 4, 8, 12 and 16 minutes. The 16 minute etched foil was very thin and etching for longer began to produce holes in the surface.

After etching, all surfaces were washed with copious amounts of deionized water and dried under a stream of compressed air before surface modification.

Surface modification

Silane modification was carried out using a combination of previously reported methods.[14,22] The surfaces were placed in a 1.0 wt% methanol (Riedel-de Haën) solution of $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$ (FAS-17) (Aldrich), which had been hydrolyzed by the addition of a threefold molar excess of water. The metal was left in this solution for 1 hour and then placed in an oven at 140 °C for 1 hour.

Surfaces to be thiol modified were coated with a 20 nm layer of sputtered gold, applied with an Edwards E306A vacuum coating system ($1–2 \times 10^{-6}$ torr). Deposition rate was kept low (0.2 nm/s) to minimise non-uniformity in the coating. They were then placed in a 1 mM dichloromethane (Riedel-de Haën) solution of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol (HDFT) (Fluka) overnight. They were removed, rinsed with dichloromethane and blown dry with compressed air. Thiol treatment of etched Cu with no gold overlayer followed the same general procedure except that the thiol treatment was carried out within 1 minute of etching to minimise surface oxidation.

Electroless galvanic deposition

A sacrificial copper layer was electrodeposited onto titanium by applying 2 V potential difference between a titanium cathode and a copper counter electrode in a 0.05 M $CuSO_4$ solution (Aldrich) for 90 minutes. The coated sample was then immersed in a 0.01 M $AgNO_3$ (99.8%, BDH) solution for 20 seconds, washed, dried and immersed in a 1×10^{-3} M HDFT dichloromethane solution for 20 minutes. It was then rinsed with dichloromethane and dried.

Scanning Electron Microscopy (SEM) was performed on a JEOL 6500 FEGSEM operating at 10 kV accelerating voltage. Roughness factors were calculated from SEM images from a Hitachi TM1000 desktop SEM operating at 15 kV accelerating voltage and using Image-pro plus version 4.5.

Contact angle measurements

Sessile contact angles were recorded with an FTA200 contact angle measuring instrument using 3.5 μl droplets. It has been shown previously that trends measured within sessile drop contact angles are similar to trends observed for both the advancing and receding angles.[31] For each sample twenty four individual measurements were made at points that were spread over the full surface. To reduce the effects of outliers in the data set we have taken a very conservative approach and automatically removed the top and bottom 7 values before calculating the mean (μ) and standard deviation (σ) which are quoted throughout as $\mu \pm \sigma$. This approach gives values that are normally distributed about the mean. However, in order to allow comparison with some parts of the literature we have also reported maximum values as ''up to x°'', since maximum values are often quoted. In general we have tried to avoid this approach since, for samples where the values are normally distributed, the maximum value recorded must necessarily increase with the number of measurements taken. This is because taking larger numbers of measurements increases the probability of encountering high value outliers. For example, $>2\%$ of the values will lie $>2\sigma$ above the mean, so even taking relatively modest numbers of measurements (*e.g.* 25) will give a high probability that a value at least 2σ above the mean will be recorded at some point.

Results and discussion

In order to separate the effects of changing surface texture/roughness and the nature of the chemical modifier it is necessary to apply different modifying layers to surfaces with the same texture. Although silane modification of Ti and Zn have been reported previously,[14,22] direct comparison with thiol modification is not possible since these metals do not support stable, self-assembled monolayers with thiols in the same way as is observed for Au and Ag. However, in this study a 20 nm sputtered gold layer was applied to the chemically etched Ti, Fe and Zn samples to make the surfaces fully compatible with thiol coating. A thickness of 20 nm was chosen because it was expected to be sufficiently thin that it would not significantly modify the texture of the surface but sufficiently thick that a continuous layer would form[32,33] that would react with thiols. Fig. 1 compares sessile contact angles of a series of Ti samples which were etched for different times, to alter their roughness, and were then either silane treated directly after etching (as previously described) or were gold coated and then treated with the polyfluorothiol (HDFT) modifier.

It is clear from Fig. 1 that, on average, the contact angles for the silane treated Ti samples were higher than the thiol-coated samples. This was also the case for Zn, where a series of samples with different etching times gave average contact angle values of 150.1° and 142.1° for silane and thiol treated surfaces, respectively.

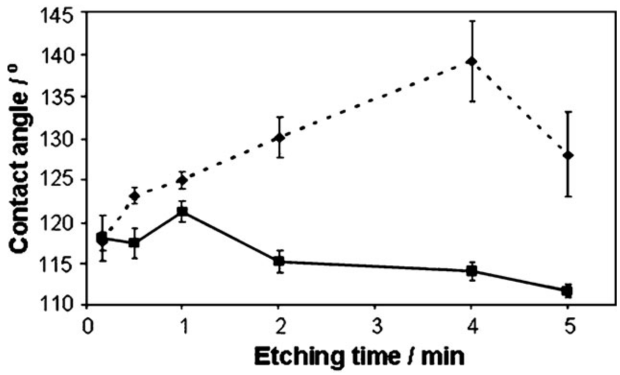

Fig. 1 Variation of contact angle of Ti which was etched for the times shown before being either Au-coated and treated with thiol (■) or directly treated with silane (◆), error bars are $\pm 2\sigma$.

To eliminate the possibility that the lower contact angle in the thiolated samples was due to some form of surface modification associated with the sputtered Au coating, rather than the effect of the different surface modifiers used, comparative experiments on etched and etched/Au-coated Cu samples were carried out. Since thiols will bind directly to Cu[34–36] (although less strongly than to Au) the etched Cu samples could be treated either directly with thiol or gold-coated before thiol modification. This gave two samples for which the only difference was the additional gold-coating step. Interestingly, even simple direct thiol treatment of a freshly etched Cu surface gave a superhydrophobic surface, with higher contact angles than any of the other etched metal data in the literature ($\theta = 160.9° \pm 1.2°$, θ up to $= 165.0°$). These surfaces also showed a low roll-off angle (α) of $< 1°$ which is an important feature of a superhydrophobic material. Moreover, the surfaces had a mirror-like appearance when viewed obliquely under water. We have previously shown that this effect is due to the presence of an air layer between the water and roughened surface found in superhydrophobic Cassie-Baxter surfaces.[15] These etched/thiolated Cu surfaces were sufficiently stable (no detectable changes for >24 hours) that even without Au coating a reliable contact angle of $160.9° \pm 1.2°$ could be measured. The etched Cu samples which were gold-coated before treatment with HDFT had contact angles of $\theta = 160.0° \pm 0.8°$ (θ up to 166.9°) and roll-off angle $<1°$, so it can be concluded that the sputtered coating has a negligible effect on the surface texture, which has previously been demonstrated.[32]

These Cu results demonstrate that it is possible to obtain superhydrophobic metal surfaces by first etching the surface to create an appropriate texture and then applying a sputtered Au layer which facilitates thiol surface modification without perturbing the surface morphology. Although the test system was Cu, the ability to separate the roughening and surface modification steps suggests that it might be possible to obtain extremely hydrophobic coatings on other metals by retaining the Au/thiol modification step and varying the etching conditions to optimize the surface texture.

The higher contact angles obtained for roughened Zn and Ti with silanes rather than Au/thiol modification might suggest that silane modification would be a more promising surface modification method than Au/thiol treatment, but large scale industrial application of silane modification, which involves prolonged exposure and heating, is impractical. On a more fundamental level, Fig. 1 shows that the scatter on the silane data was significantly higher than that with thiols, which makes it extremely difficult to discern trends in the data. For example, the large uncertainty at the longer etching times makes it impossible to determine whether the data rise to a peak before falling or tend to a plateau contact angle value. It is difficult to measure contact angles with a precision of better than a few degrees but the additional scatter in the data ($\sigma = 2.6°$ for silane but 1.5° for thiol) does appear to be associated with real differences in the properties of the surfaces at different measurement points. This is most apparent for etched

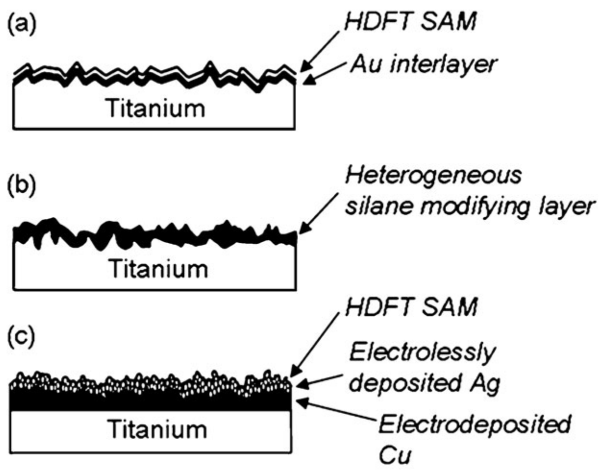

Fig. 2 Illustration of the 3 modification surface methods used here. (a) Etch followed by application of a Au interlayer and subsequent thiol treatment. (b) 'Etch and coat' using silane modifier. (c) Deposition of a sacrificial copper layer followed by electroless deposition of a heavily textured Ag layer and, finally, application of thiol modifier.

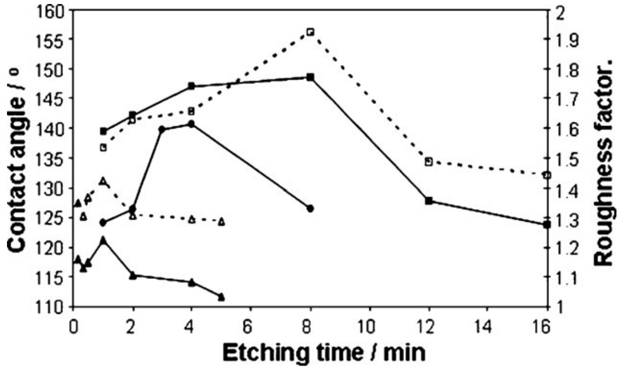

Fig. 3 The contact angle (filled marker) and roughness factors (empty markers) for titanium (△), iron (○) and zinc (□) samples etched for the times shown before being coated with a 20 nm Au layer and treated with HDFT polyfluorothiol.

Zn surfaces treated with silane, which show mirror-like reflections on some parts of the surface when viewed obliquely under water, but also displayed regions of low reflectivity, indicating loss of the Cassie-Baxter behaviour in those areas.

The higher uniformity of the surfaces treated with thiol is not surprising. The chemistry of thiols favours formation of uniform coatings,[25] Fig. 2(a), because each molecule is able to attach directly to the surface by formation of a covalent bond. In contrast, it has been reported that silanes attach only at a minority of surface hydroxyl groups,[24,37] and this, coupled to the fact that the FAS-17 used here also self-condenses,[38] strongly suggest that the silane coating may well be in the form of a non-uniform polymer mat, Fig. 2(b), that is anchored to the surface at a small number of random points, thus giving non-uniform surface coverage. It is notable that the trends in contact angle with increasing etching time shown in Fig. 1 appear to be different for the two coatings, which suggests that they may be due to effects other than a simple difference in their surface energies.

Irrespective of the chemical reasons for the lower uncertainty in the contact angle measurements with gold-sputtered thiol modified surfaces, the fact that contact angle measurement with $\sigma < 2^\circ$ can be made has allowed us to systematically investigate the effect of roughness, created by wet etching, on the wettability of metals. In previous studies of metal etching, very limited sets of etching times were used, presumably because the natural assumption was that it was only necessary to establish how much time was needed for the etching to roughen the surface sufficiently. Unexpectedly, we have found that for all three metals tested the contact angles do not increase steadily to a plateau with increased etching time but instead reach a maximum from which they decline with longer etching times, as shown in Fig. 3.

The origin of this trend can be observed in the SEM images of the surfaces at different etch times shown in Fig. 4. Fig. 4(a) and 4(c) show Ti and Zn surfaces at early etching times. These surfaces give higher contact angles than those in Fig. 4(b) and 4(d), which had more prolonged etching. It is clear from the images that as the etching time is increased the size of the etched crystal faces also increases so the fraction of the surface with domain boundaries gets much smaller.

Since the SEM images allowed only qualitative comparisons between the roughness of the various surfaces it was still necessary to establish that it was the roughness on these length scales that was determining the hydrophobicity. As a first step, the roughness factor, *r*, was determined by recording cross sectional SEM images and measuring the ratio of the straight distance between two points on the surface against the length of the path following the surface texture, as shown in Fig. 5. The measured *r* values for a series of etching times are plotted along with the corresponding contact angles for Zn and Ti in Fig. 3 and there is clearly a close qualitative correlation between the two parameters. The Fe surfaces were heterogeneous on the micro-scale, comprising very rough patches 10's of μm in diameter among areas of similar dimension which were less heavily textured. This made it difficult to generate unbiased roughness figures since the value fluctuated significantly depending on the particular length segment chosen.

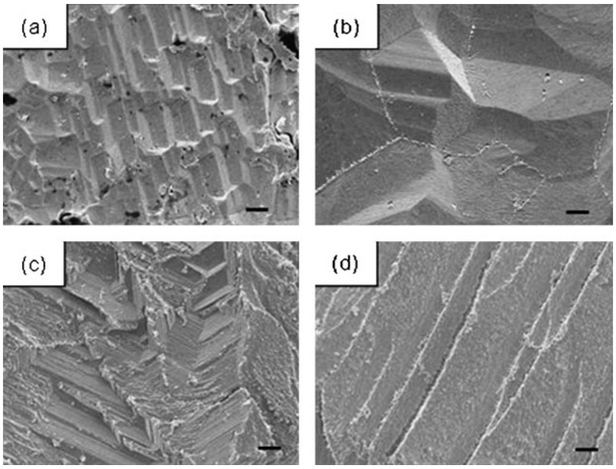

Fig. 4 SEMs of (a) Ti etched with HF for 10 seconds, (b) Ti etched with HF for 6 minutes, (c) Zn etched with HCl for 8 minutes and (d) Zn etched with HCl for 12 minutes. Scale bars are 1 μm.

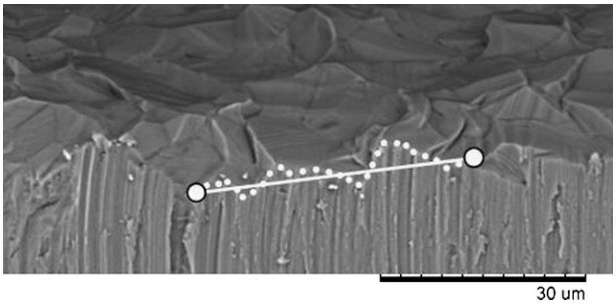

Fig. 5 SEM of a cross-section of Ti etched with HF for 2 minutes, illustrating the method used to determine the roughness factor, *r*.

It is possible to make a quantitative analysis of the roughness data if water droplets deposited on the surfaces are in the Wenzel state[39] because the measured contact angle (θ^*) can then be related to the Young's angle (θ) and the roughness factor (r) by eqn (1).

$$\cos \theta^* = r \cos \theta \qquad (1)$$

The fact that the droplets were pinned even when the surfaces, whose contact angles are shown in Fig. 3, were held vertically suggests that they were in a Wenzel state.[40] Consistent with this, a plot of cos θ^* against r (not shown) is a straight line with a correlation coefficient of 0.87. Substituting values for r into eqn (1) gives a value for θ, the contact angle at zero roughness on these metal surfaces, of $115.2 \pm 4.1°$. This value closely matches the value we measured for HDFT on flat gold foil, $108.4 \pm 2.2°$ and is close to the contact angle of HDFT on an atomically flat gold (111) surface of (119°).[41]

These results suggest that the behaviour of silane-coated surfaces is more complex than it might appear. The θ value for the thiol treated surfaces is close to the highest known value for a smooth surface, suggesting that the thiol coatings do provide a surface energy near this limit. However, as discussed above, at least some parts of the silane coated surfaces have higher contact angles than thiolated surfaces applied to the same roughened metal substrate. This suggests that either the surface energy of the silane coating in these areas is lower than even the extremely low values obtained with the polyfluorothiols or that the silane adds to the effective "roughness" of the surface. Since it is unlikely that the surface energy of the silanes is lower than well-ordered fluoroalkyl surfaces provided by the thiols it is proposed that the polymer coating is either not of uniform thickness[42] or the chemical properties of the surface are not the same at every point on the surface, as illustrated in Fig. 2(b). In contrast the 20 nm Au coating follows the inherent topography of the roughened metal,[32,33] as does the thiol monolayer which binds to it,[24] Fig. 2(a). Although the increased apparent roughness given by silane coating, whatever its origin, does increase the hydrophobicity of the surfaces it is probably also associated with the larger scale non-uniformity which is observed and is a disadvantage when a surface coating with known and consistent performance is required. This is one reason that thiol modification would be the preferred option provided the thiolated surfaces can be made sufficiently hydrophobic.

Despite the fact that HDFT is extremely effective at lowering the surface energy we have found that, even after optimising the etching times, treating Zn, Fe and Ti with HDFT gave only one sample (Zn, 8 minute etch) with a contact angle ($\theta = 148.6° \pm 2.6°$, θ up to 157.1°) which was above the $>150°$ threshold for a superhydrophobic surface, unfortunately this surface showed a large roll-off, $\alpha > 90°$. However, the contact angle values for etched Cu were much higher, along with a significantly lowered roll-off angle, compared to the other metals investigated, which raises the possibility that as an alternative to etching Ti or Fe surfaces, for example, these metals could be coated with Cu which would then be etched, Au-coated and then modified with thiol.

Two potential practical problems with this approach are in finding etching conditions that will provide the necessary roughness but not completely remove the Cu layer, and the need to apply a sputtered gold layer which immediately limits the size of objects that can be treated.

To circumvent these problems we have developed a variation on this approach in which a Cu layer is applied over the substrate but then, rather than etching, it is roughened by deposition of a heavily textured Ag (or Au) over-layer, as shown in Fig. 2(c). This builds on our previous observation that simply immersing Cu surfaces in solutions of Au(III) or Ag(I) salts results in a spontaneous electroless Galvanic deposition of a very rough textured metal layer that can be treated with HDFT to produce extremely hydrophobic surfaces with $\theta > 173°$.[15]

Fig. 6 shows a SEM image of a *ca.* 30 μm thick Cu layer prepared by slow electrodeposition onto Ti. This layer is not completely smooth, Fig. 6(a), indeed the surface texture is similar to the etched surfaces shown in Fig. 4, but clearly does not have the heavily textured fractal structure which is shown when Cu is electrochemically grown on a support.[43,44] However, as shown in Fig. 6(b), immersion of the sample into an $AgNO_3$ solution results in deposition of a silver layer with much smaller features on top of the μm dimension features of the underlying Cu, creating a "double roughness" of the type associated with extremely hydrophobic surfaces.[45] It is clear that this simple Ag deposition step has a much larger effect on the surface texture than changing etching times, as shown in Fig. 3, for example. The introduction of this second texture to give double roughness has a very marked effect on the surface properties. Following modification with HDFT the contact angle rises to $\theta = 165.5° \pm 2.2°$, θ up to 168.9° and roll-off angle $<1°$, which is similar to the results previously reported for the best coatings on copper foil. This method appears to be

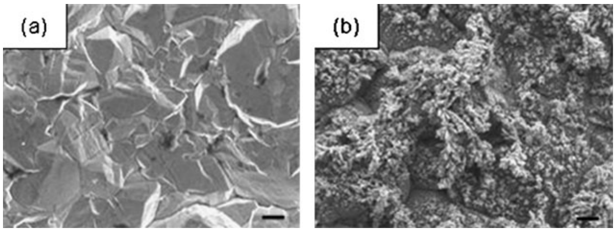

Fig. 6 SEMs of (a) electrodeposited Cu on Ti and (b) a section of the same sample as in (a) following electroless Galvanic deposition of Ag onto the sacrificial Cu layer. Scale bars are 1 μm.

independent of the material onto which the copper layer is deposited and thus provides a very general route to creating ultrahydrophobic surfaces since any substrate that can be copper coated, whether by sputtering or electrodeposition, can be treated.

Conclusions

It has been shown that the use of a gold sputtering/thiol modification route can separate out the effect of chemical modification from the effect of roughening. It is noted that thiols give surfaces with much more uniform properties over large areas compared to silanes, which are prone to self-condensation and non-uniform surface attachment. This improved the basis for investigation of the effect of wet etching of metals over an extended time range which clearly showed that the contact angle increased to a maximum before falling, an observation which silane modification appears to have masked previously. This trend seems to be totally independent of the nature of the metal.

Even using optimised etch times, a Au interlayer which was thin enough to maintain the surface roughness and a very low surface energy polyfluorothiol modifier, the contact angles achieved with thiol modification were lower than those found for silane modification of the same roughened metals. It is suggested that silane modification gives an increase in apparent roughness over thiol modifiers which follow the topography of the underlying metal. However, despite their generally higher contact angles, silane surfaces were much less uniform with respect to their contact angles than those which were thiol treated and were less straightforward to apply. For these reasons we chose to work on improving thiol modified systems. Although no combination of etching, Au coating and thiol modification was capable of producing surfaces at the higher ends of the superhydrophobic range for Ti, Zn and Fe it was found that application of a sacrificial copper layer followed by an electroless Galvanic deposition method gave surfaces equal to the best previously reported. This very general method for the preparation of superhydrophobic surfaces on metals is sufficiently simple and inexpensive to be suitable for application on industrial scales, for example in marine or aeronautical engineering.

References

1. X. J. Feng and L. Jiang, *Adv. Mater.*, 2006, **18**, 3063–3078.
2. W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**, 1–8.
3. C. Neinhuis and W. Barthlott, *Ann. Bot.*, 1997, **79**, 667–677.
4. P.-G. de Gennes, F. Brochard-Wyart and D. Quere, *Capillarity and Wetting Phenomena; Drops, Bubbles, Pearls, Waves*, Springer, New York, 2003.
5. D. Oner and T. J. McCarthy, *Langmuir*, 2000, **16**, 7777–7782.
6. T. Baldacchini, J. E. Carey, M. Zhou and E. Mazur, *Langmuir*, 2006, **22**, 4917–4919.
7. Y. Coffinier, S. Janel, A. Addad, R. Blossey, L. Gengembre, E. Payen and R. Boukherroub, *Langmuir*, 2007, **23**, 1608–1611.
8. L. C. Gao and T. J. McCarthy, *J. Am. Chem. Soc.*, 2006, **128**, 9052–9053.
9. K. Q. Peng, Y. J. Yan, S. P. Gao and J. Zhu, *Adv. Funct. Mater.*, 2003, **13**, 127–132.
10. K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, G. H. McKinley and K. K. Gleason, *Nano Lett.*, 2003, **3**, 1701–1705.
11. Y. Li, X. J. Huang, S. H. Heo, C. C. Li, Y. K. Choi, W. P. Cai and S. O. Cho, *Langmuir*, 2007, **23**, 2169–2174.
12. L. B. Zhu, Y. H. Xiu, J. W. Xu, P. A. Tamirisa, D. W. Hess and C. P. Wong, *Langmuir*, 2005, **21**, 11208–11212.
13. Z. G. Guo, F. Zhou, J. C. Hao and W. M. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 15670–15671.
14. B. T. Qian and Z. Q. Shen, *Langmuir*, 2005, **21**, 9007–9009.
15. I. A. Larmour, S. E. J. Bell and G. C. Saunders, *Angew. Chem., Int. Ed.*, 2007, **46**, 1710–1712.
16. S. T. Wang, L. Feng, H. Liu, T. L. Sun, X. Zhang, L. Jiang and D. B. Zhu, *ChemPhysChem*, 2005, **6**, 1475–1478.
17. J. T. Han, Y. Jang, D. Y. Lee, J. H. Park, S. H. Song, D. Y. Ban and K. Cho, *J. Mater. Chem.*, 2005, **15**, 3089–3092.
18. S. Chen, C. H. Hu, L. Chen and N. P. Xu, *Chem. Commun.*, 2007, 1919–1921.
19. Y. Li and G. Q. Shi, *J. Phys. Chem. B*, 2005, **109**, 23787–23793.
20. F. Shi, Y. Y. Song, H. Niu, X. H. Xia, Z. Q. Wang and X. Zhang, *Chem. Mater.*, 2006, **18**, 1365–1368.
21. M. Thieme, R. Frenzel, S. Schmidt, F. Simon, A. Hennig, H. Worch, K. Lunkwitz and D. Scharnweber, *Adv. Eng. Mater.*, 2001, **3**, 691–695.
22. M. N. Qu, B. W. Zhang, S. Y. Song, L. Chen, J. Y. Zhang and X. P. Cao, *Adv. Funct. Mater.*, 2007, **17**, 593–596.
23. Z. Guo, J. Liang, J. Fang, B. Guo and W. Liu, *Adv. Eng. Mater.*, 2007, **9**, 316–321.
24. D. K. Schwartz, *Annu. Rev. Phys. Chem.*, 2001, **52**, 107–137.
25. A. Ulman, *Chem. Rev.*, 1996, **96**, 1533–1554.
26. M. Buck, M. Grunze, F. Eisert, J. Fischer and F. Trager, *J. Vac. Sci. Technol. A-Vac. Surf. Films*, 1992, **10**, 926–929.
27. R. Heinz and J. P. Rabe, *Langmuir*, 1995, **11**, 506–511.
28. D. S. Karpovich and G. J. Blanchard, *Langmuir*, 1994, **10**, 3315–3322.
29. S. Frey, K. Heister, M. Zharnikov, M. Grunze, K. Tamada, R. Colorado, M. Graupe, O. E. Shmakova and T. R. Lee, *Isr. J. Chem.*, 2000, **40**, 81–97.
30. S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 2000, **12**, 1315–1328.
31. M. Taniguchi and G. Belfort, *Langmuir*, 2002, **18**, 6465–6467.
32. R. Chopra, F. Podczeck, J. M. Newton and G. Alderborn, *Particle & Particle Systems Characterization*, 2002, **19**, 277–283.
33. D. R. Gabe, *Principles of Metal Surface Treatment and Protection*, Pergamon Press, Oxford, 2nd edn., 1978.
34. R. Haneda and K. Aramaki, *J. Electrochem. Soc.*, 1998, **145**, 1856–1861.
35. R. Haneda, H. Nishihara and K. Aramaki, *J. Electrochem. Soc.*, 1997, **144**, 1215–1221.
36. F. Sinapi, I. Lejeune, J. Delhalle and Z. Mekhalif, *Electrochim. Acta*, 2007, **52**, 5182–5190.
37. X. L. Zhao and R. Kopelman, *J. Phys. Chem.*, 1996, **100**, 11014–11018.
38. S. Suzuki, A. Nakajima, N. Yoshida, M. Sakai, A. Hashimoto, Y. Kameshima and K. Okada, *Langmuir*, 2007, **23**, 8674–8677.
39. R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988–994.
40. D. Quere, A. Lafuma and J. Bico, *Nanotechnology*, 2003, **14**, 1109–1112.
41. T. Nishino, M. Meguro, K. Nakamae, M. Matsushita and Y. Ueda, *Langmuir*, 1999, **15**, 4321–4323.
42. S. Li, H. Xie, S. Zhang and X. Wang, *Chem. Commun.*, 2007, 4857–4859.
43. D. B. Hibbert and J. R. Melrose, *Phys. Rev. A*, 1988, **38**, 1036–1048.
44. N. J. Shirtcliffe, G. McHale, M. I. Newton and C. C. Perry, *Langmuir*, 2005, **21**, 937–943.
45. Y. H. Xiu, L. B. Zhu, D. W. Hess and C. P. Wong, *Langmuir*, 2006, **22**, 9676–9681.