One-Step Deposition Process to Obtain Nanostructured Superhydrophobic Thin Films by Galvanic Exchange Reactions

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Abstract

Superhydrophobic thin films of silver were fabricated on copper substrates by galvanic ion exchange reactions in a one-step process by immersing copper substrates in silver nitrate solution containing fluoroalkylsilane in different quantities. The X-ray diffraction (XRD) analyses confirmed the formation of silver films on copper substrates and the fractal-like morphological features of the silver films were confirmed using scanning electron microscopy (SEM). The contact angle of water on these surfaces is found to be greater than $165°$, demonstrating water repellency with water drops rolling off the surfaces. The X-ray photoelectron spectroscopy (XPS) depth profile confirms the presence of fluorine in the silver films.

Keywords

Galvanic exchange reactions, superhydrophobic thin films, one-step process

1. Introduction

Superhydrophobicity is a property that describes the non-wetting characteristics of a material surface, which, in turn, is termed a superhydrophobic surface. The water contact angle (CA) on such surfaces is usually greater than $150°$ with a very low contact angle hysteresis. Certain natural tissues, among them the surface of lotus leaves, are the most obvious examples of inherent superhydrophobic and selfcleaning properties,

sometimes known popularly as the 'Lotus effect'. The so-called 'Lotus effect' is due to the presence of a rough micro/nanostructure covered with low surface energy waxy materials [1–4]. The rough structure allows for air to be trapped under a water droplet in the gaps of the micro/nanostructure, resulting in a heterogeneous surface composite, where air and the waxy tissue provide a very low surface energy, enhancing the contact angle of the rough structure and reducing the contact area of the water drop with the surface. Wettability is a fundamental property of solid surfaces which plays an important role in daily life and several industrial applications [5]. A recent book entitled '*Superhydrophobic Surfaces*' edited by A. Carré and K. L. Mittal illustrates several preparation techniques and the various applications of superhydrophobic surfaces [6]. Recently, we have demonstrated that superhydrophobic nanostructured surfaces may also play an important role in anti-icing effects, which may lead to important applications such as coatings for electrical cables, insulators, aircraft wings, ship hulls, glass structures, windshields, etc. [7]. Nature has taught us that in making superhydrophobic surfaces, two essential factors are involved, namely, optimized surface roughness and low surface energy material. Inspired by surface engineering found in nature, and using the concepts provided by the Wenzel and Cassie–Baxter models of wetting [8, 9], the methodologies for preparing superhydrophobic surfaces can be generally categorized into the 'top-down' and 'bottom-up' approaches as a first step to create a specific surface roughness. Top-down approaches encompass lithographic and template-based techniques [10], laser ablation technique [11] and plasma treatment of the surfaces [12, 13]. Bottom-up approaches mostly involve self-assembly and self-organization [14], such as chemical bath deposition (CBD) [15, 16], chemical vapor deposition (CVD) [17] and electrochemical deposition [18]. Such surfaces are usually coated with a low surface energy material as a second step to eliminate or reduce further interactions with water. In the last two years we have fabricated several superhydrophobic surfaces using diverse methods which demonstrated water roll-off properties [7, 16, 19–24]. All the above-mentioned studies involve two-step processes where in the first step a rough surface is created and in the second step, the rough surface is 'passivated' by coating with low surface energy molecules or thin films. Among the low surface energy materials used for surface passivation, fluoroalkylsilanes (FAS), which are terminated with low surface energy groups such as CF_3, CF_2, CF etc., are widely used [23, 25–27]. We have previously reported the formation of a superhydrophobic coating on a chemically patterned aluminum surface using FAS and evaluated its thermal stability [23]. Silver

films have been previously rendered superhydrophobic *via* a two-step approach by electroless deposition [28]. Very recently, we have demonstrated superhydrophobicity on silver thin films deposited on copper surfaces by galvanic exchange reactions followed by passivation with stearic acid (SA) [19]. However, a superhydrophobic coating consisting of only a single layer of an organic molecule such as SA is not very stable even against the frictional force caused by water flow and, therefore, may not be suitable for a prolonged application. Moreover, as mentioned before, the methods used involve two-step processes. Incorporation of the low surface energy molecules throughout the films during the process of rough pattern generation would lead to a superhydrophobic surface in a single step. Such coatings might be of great importance where environmental erosion is encountered. In this communication, we report on the fabrication of superhydrophobic silver films on copper substrates in a one-step process, with the low surface energy FAS molecules distributed throughout the deposited film. A two-step process was also performed for comparison by depositing silver films first and then passivating with FAS.

2. Experimental

One-inch-square copper substrates were cleaned with soap to remove any oil or grease and then further treated with a very dilute nitric acid solution to remove the native oxide layer. The superhydrophobic coatings of thin silver films were deposited by a one-step process as well as by a two-step process. In the first method, the copper substrate was immersed in 20 ml of 50 mM aqueous AgNO3 solution mixed with varying quantities of FAS molecules in ethanol solution for a period of 4 min. The molecular percentage (mol%) of FAS with respect to Ag+ ions (FAS FAS+Ag+ × 100%*)* was varied from 1 to 28 mol%. In the second method, copper substrates were first immersed in 20 ml of 50 mM aqueous AgNO3 solution for 4 min for the silver deposition and then passivated by immersing in 50 mM ethanolic FAS solution for 30 min after drying the silver films at 70◦C for more than 10 h. The X-ray diffraction (XRD) analysis of the silver coated surfaces was carried out using a Bruker D8 Discover system. The surface chemical compositional analyses and depth profiling were performed using X-ray photoelectron spectroscopy (XPS) (VG ESCALAB 220iXL). The XPS spectra were collected using an Al Kα (1486.6 eV) X-ray source. The depth profiles of the samples prepared in the onestep and two-step processes were carried out by 3 keV Ar+ ion sputtering to monitor the FAS incorporation in the silver films. The morphological characterization was

performed using a JEOL (JSM 6480 LV) scanning electron microscope (SEM). The wetting characteristics of the sample surfaces (contact angle measurements) were evaluated at room temperature using a First Ten Angstroms contact angle goniometer following a standard and commonly used experimental procedure as reported in the literature [7, 29]. In this method, a water drop of volume ~8 μl was suspended from a needle and brought in contact with the superhydrophobic surfaces.The contact angle hysteresis was calculated from the measured advanced and receding angles of water drops, suspended from a needle, in contact with a moving superhydrophobic surface [7].

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns of (a) copper substrates and (b) silver films deposited on copper substrates using aqueous silver nitrate solution
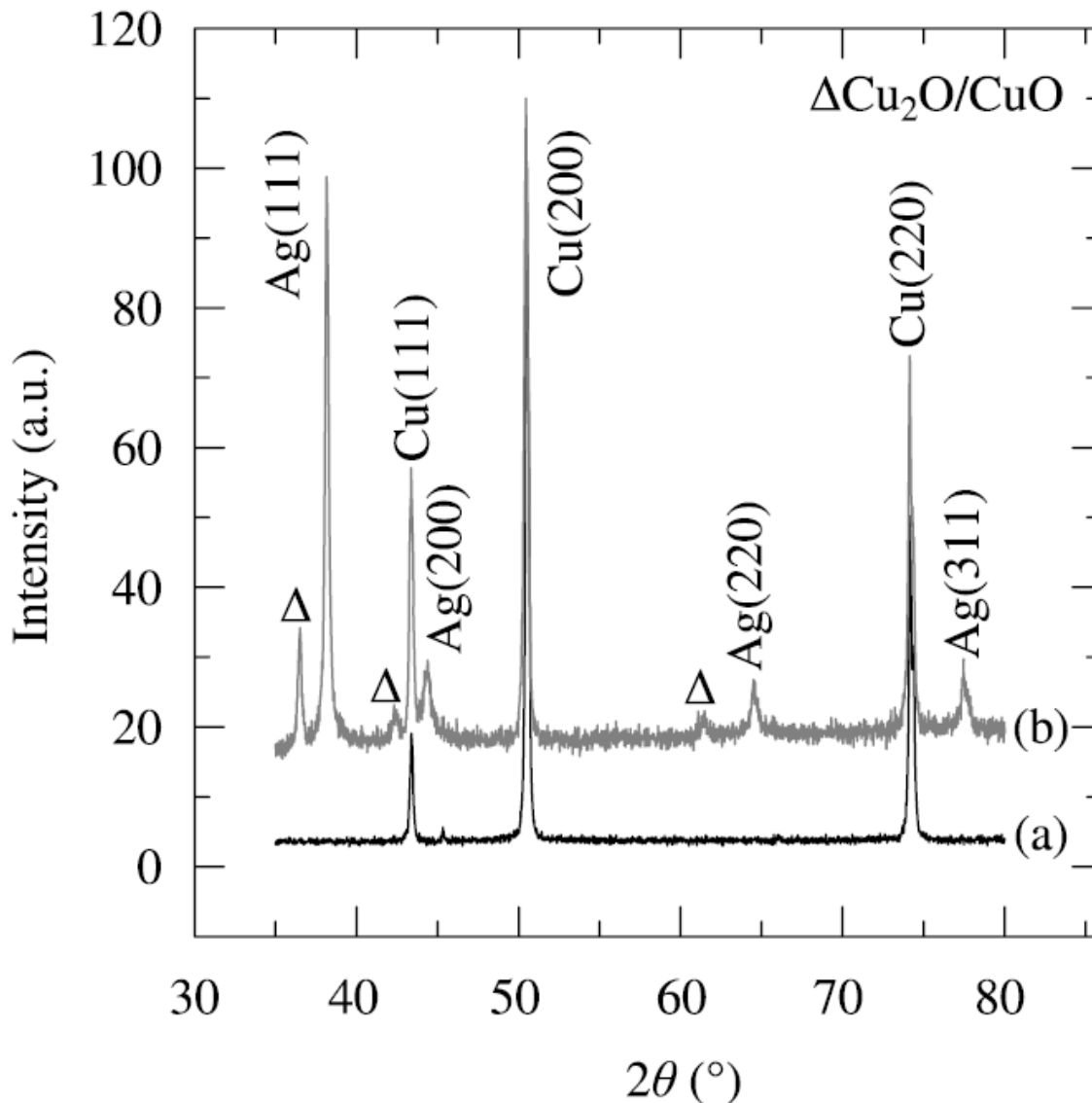
Figure 1. XRD patterns of (a) copper substrates, (b) Ag films deposited by galvanic exchange reactions on copper substrates from the silver nitrate solution with FAS.

in the presence of FAS molecules. In the 2θ scan range of 35–80◦ (Fig. 1(a)) copper substrates show characteristic peaks of Cu(111), Cu(200) and Cu(220) at 43.4◦, 50.5◦ and 74.2◦, respectively, which are in good agreement with the bulk copper crystallographic data [30]. Fig. 1(b) shows the XRD pattern of the silver deposited on copper substrates by galvanic ion exchange reactions with FAS molecules in the silver nitrate solution. The molar percentage of the FAS molecules was 2 mol%. The deposited thin films of silver show the characteristic peaks of Ag(111), Ag(200), Ag(220) and Ag(311) at 38.2◦, 44.4◦, 64.5◦ and 77.5◦, respectively. These peaks appear at slightly

higher diffraction angles as compared to the bulk silver diffraction data [31]. The lattice parameter of silver in our film is ~1% smaller than in the bulk silver as calculated from the peak of Ag(111). The two peaks at 36.5° and 42.41° are due to the formation of cubic copper oxides (Cu2O/CuO) in the crystalline phase, an observation complemented by the blackened appearance of the deposited films [32]. However, the black appearance of the surface could also be caused by the presence of nanostructured silver particles. It has been observed that the intensity of the oxide peaks decreases with an increase in the FAS concentration in the solution (data not shown here).

Figure 2 shows the SEM image of the silver films deposited on copper substrates by galvanic ion exchange reactions. The surface morphology shows a fractal structure with resemblance to a structure previously reported in our recent work [19]. The morphological features observed in the present work, however, remain similar with no noticeable changes when the silver films were deposited with FAS in
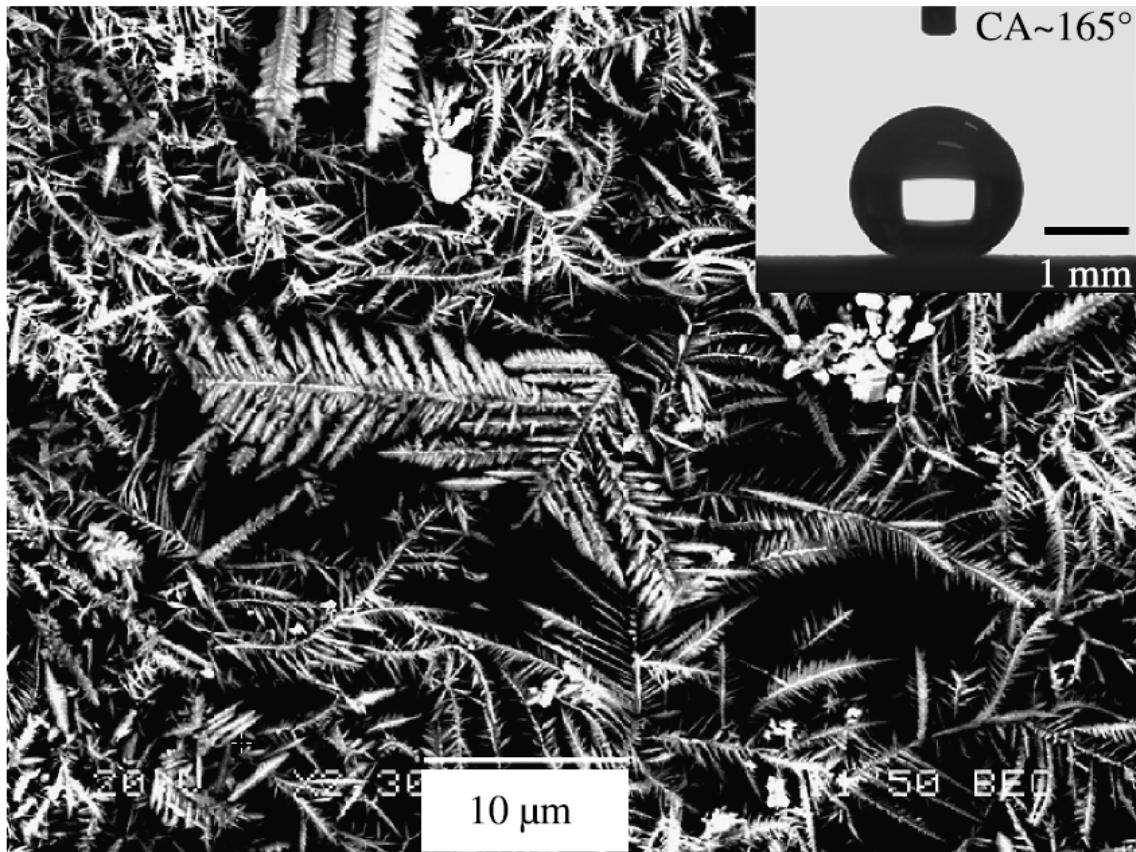
Figure 2. SEM image of a silver film deposited on a copper substrate by galvanic exchange reactions. The inset shows a drop of water on this surface prepared by either the one-step or two-step process.

the AgNO3 solution. The inset of Fig. 2 shows a water drop on such fractal surface prepared by either the one-step process with 2% FAS in the AgNO3 solution or twostep process (FAS passivation after Ag coatings). The contact angle (CA) of water obtained is around 165◦ with the water drops rolling off the surfaces easily even with the slightest tilt of the surface. The CA value is found to be in good agreement with the literature values as most of the reported CA values on FAS passivated surfaces are in the range of 150◦ to 170◦ [23, 25–27]. The roll-off property was found to be present on all surfaces prepared by varying the quantity of FAS molecules in the silver nitrate solution between 1 mol% and 28 mol%. The detailed study of the morphological change of the silver films with the increase of FAS content in the AgNO3 solution is in progress and will be published elsewhere. The purpose of fabricating superhydrophobic films in a one-step process is to maintain the superhydrophobicity through the entire thickness of the film unlike the FAS monolayers self-assembled on the silver surface in a two-step process which are usually prone to wear even with the friction caused by a simple flow of water. XPS depth profiles were obtained, in order to confirm the presence of FAS molecules in the superhydrophobic films prepared by both one-step and two-step processes. Figure 3(a) shows the survey spectra of the surfaces of a FASincorporated silver thin film on a copper substrate prepared by the one-step process and a FAS-passivated silver film prepared by the two-step process. The spectra confirm the presence of all the elements of interest, namely, C, F, O, Ag and Cu. The binding energy scales of various peaks in the spectra have been corrected for charging by situating the peak of –CF2 at 291.2 eV [7, 25, 26]. The presence of FAS
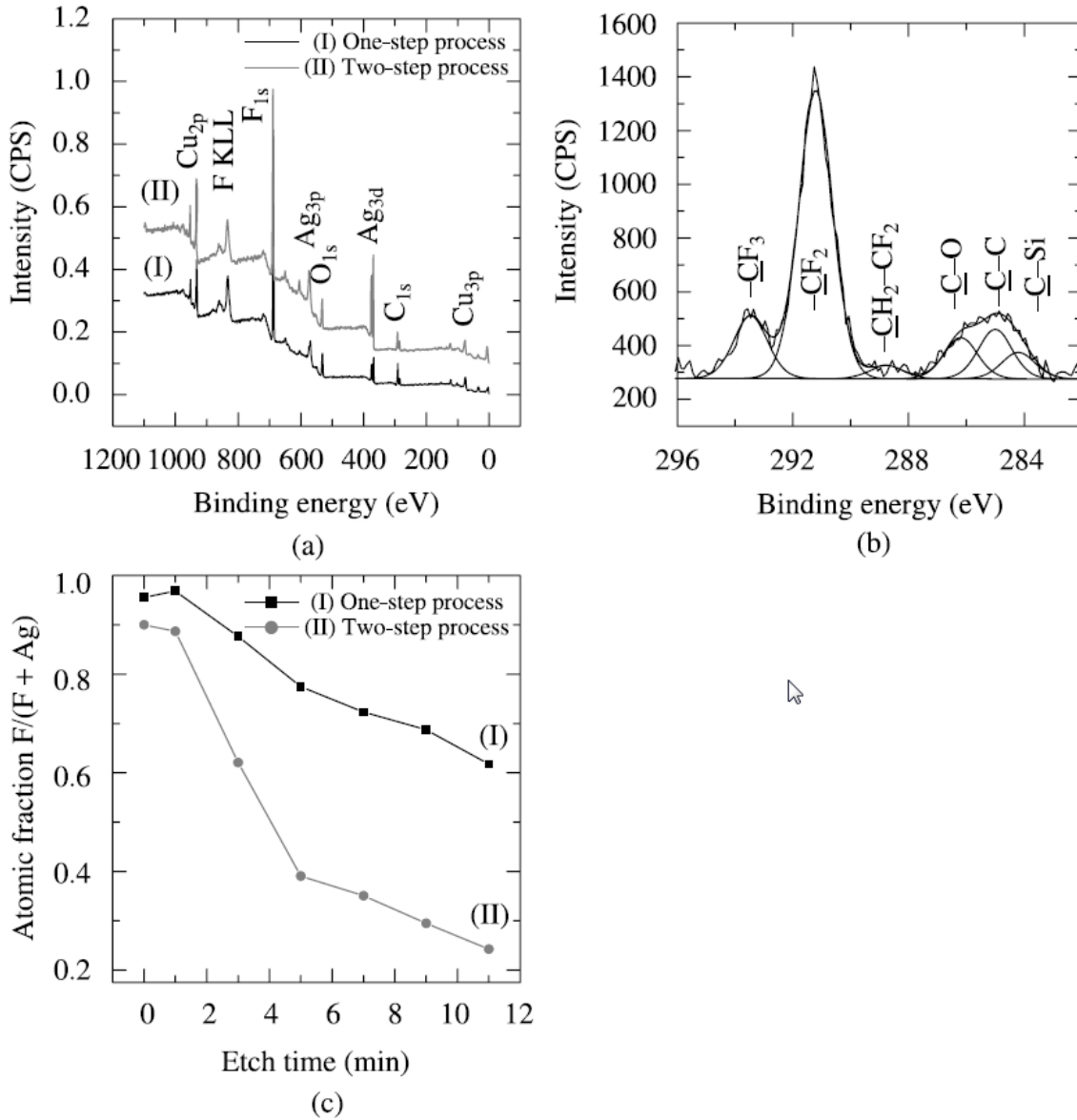
Figure 3. (a) XPS spectra of silver thin films with FAS prepared in one-step and two-step processes, (b) C1s spectrum of the silver thin film containing FAS grown in the one-step process, (c) depth profiles of F in silver thin films grown in the one-step and two-step processes.

on both surfaces is obvious from the observation of a strong F peak at 688.6 eV in both survey spectra. The high resolution C1s peak is presented in Fig. 3(b). The two distinct peaks of C1s observed at 291.2 and 285.0 eV confirm the presence of $-CF_2$ and $-C-C$ groups in the films. The presence of silver on the surface has been confirmed by the Ag3d peak noticed at 368.6 eV. The presence of other elements, namely, O and Cu is

also noted in the spectra. The C1s core level spectrum from the surface of the film deposited by the onestep process, as shown in Fig. 3(b), has been resolved into six components, namely, –CF3 (293.5 eV), –CF2 (291.2 eV), –CH2–CF2 (288.8 eV), –C–O (286.2 eV), –C–C (285 eV) and –C–Si (284.2 eV), which are found to be in good agreement with recently reported binding energies [7, 25, 26]. The high resolution spectra show that the F1s has a single peak at 688.5 eV and that the Ag3d has two peaks, Ag3d5∕2 and Ag3d3∕2 at 368.6 eV and 374.6 eV, respectively. Figure 3(c) shows the depth profile of the films deposited both by the one-step and two-step processes in terms of the atomic fraction of F with respect to Ag, (F F+Ag). It is observed that the atomic fraction of F in the film prepared by the one-step process is 0.95 whereas in the case of the two-step process this value is 0.90. The atomic fractions of F are reduced to 0.77 and 0.39 in the case of films prepared by one-step and two-steps processes, respectively, after sputtering for 5 min. These values further decrease to 0.62 and 0.24, in the films prepared by one-step and two-step processes, respectively, after sputtering for 11 min. The decay of F in the films prepared by the one-step process is much slower compared to the decay of F in the film obtained *via* the two-step process. This analysis shows that the amount of subsurface F is higher in case of the film prepared *via* the one-step process for the same period of sputtering. Therefore, it can be postulated that the superhydrophobicity of the film deposited by the one-step process would be more resistant to physical erosion. However, in the long run it is possible that erosion can cause change in surface roughness, thereby altering the superhydrophobic properties. The bonding characteristics of the FAS molecules have been analyzed by XPS from the O1s peak as presented in Fig. 4(a). The O1s peak has been deconvoluted into four peaks. The peak at 530.3 eV is due to the presence of Cu2O/CuO in the Ag films as complemented by XRD (Fig. 1(b)) [33]. The peak at 533 eV is due to the bonding of O with two Si atoms in the hydrolyzed FAS clusters. This binding
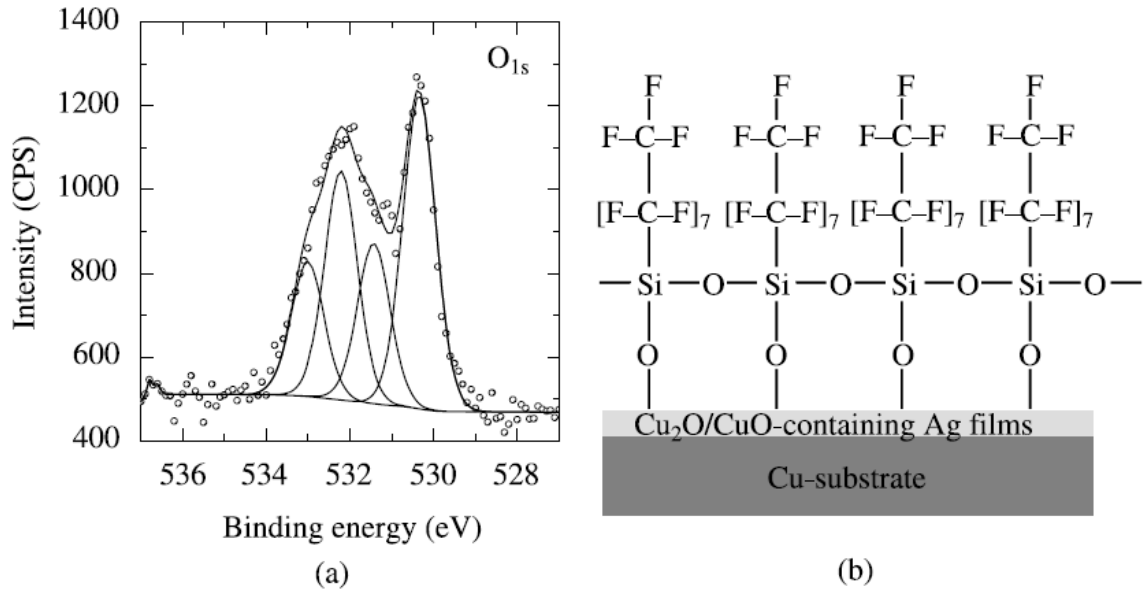
Figure 4. (a) O1s spectrum of the FAS-covered silver films grown in galvanic exchange reactions, (b) schematic of the FAS molecules bonding to silver films grown in galvanic exchange reactions.

energy value is comparable with the binding of O1s in the oxide of silicon [34]. The peak at binding energy 531.4 eV is due to the covalent bonding of O atoms linking the substrate metal and the Si in the FAS molecules. This binding energy is comparable to the binding energy of O1s in the metal silicate [35]. The peak at 532.2 eV is due to the bonding of O with Si and C atoms in the non-hydrolyzed, but embedded FAS molecules in the Ag films. The binding energy of O1s in this case is comparable to the O atoms bonded with C and Si in the hydrogenated silane molecules ((–(CH3$)$2SiC6H4SiO(CH3$)$2–)n) [36]. Unfortunately, authors have not found any information about the O1s binding energy in FAS molecules in the literature. A schematic of the bonding of FAS with the substrate is presented in Fig. 4(b) based on the O1s spectrum with three peaks at 530.34 eV (Cu–O), 531.43 eV (Si–O–M) and 533.01 eV (Si–O–Si). The Cu2O/CuO-incorporated Ag film on the Cu substrate as obtained by galvanic exchange reactions is shown in the schematic based on XRD and O1s peak from XPS analysis. The FAS molecules are bonded to the substrate metal atoms with the O atoms of the FAS molecules as presented in Fig. 4(b).

4. Conclusion

In conclusion, we have developed a novel one-step process to fabricate nanostructured superhydrophobic silver thin films deposited on a copper surface by galvanic exchange reactions with low surface energy FAS molecules distributed in-depth rather than only as a surface layer as evident from XPS depth profile. Bonding of FAS molecules has been discussed and modeled based on XPS analysis. A water contact angle greater than 165∘, leading to roll-off of water drops, has been obtained on these surfaces.

References

1. W. Barthlott and C. Neinhuis, *Planta* **202**, 1 (1997).
2. X. Gao and L. Jiang, *Nature* **432**, 36 (2004).
3. Y. Zheng, X. Gao and L. Jiang, *Soft Matter.* **3**, 178 (2007).
4. J. Huang, X. Wang and Z. L. Wang, *Nano Lett.* **6**, 2325 (2006).
5. T. Sun, L. Feng, X. Gao and L. Jiang, *Acc. Chem. Res.* **38**, 644 (2005).
6. A. Carré and K. L. Mittal (Eds), *Superhydrophobic Surfaces.* VSP/Brill, Leiden (2009).
7. D. K. Sarkar and M. Farzaneh, *J. Adhesion Sci. Technol.* **23**, 1215 (2009).
8. R. N. Wenzel, *Ind. Eng. Chem.* **28**, 988 (1936).
9. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.* **40**, 546 (1944).
10. J. Li, J. Fu, Y. Cong, Y. Wu, L. J. Xue and Y. C. Han, *Appl. Surf. Sci.* **252**, 2229 (2006).
11. M. Thieme, R. Frenzel, S. Schmidt, F. Simon, A. Hennig, H. Worch, K. Lunkwitz and D. Scharnweber,
Adv. Eng. Mater. **3**, 691 (2001).
12. V. Stelmashuk, H. Biederman, D. Slavinska, J. Zemek and M. Trchova, *Vacuum* **77**, 131 (2005).
13. S. H. Kim, J. H. Kim, B. K. Kang and H. S. Uhm, *Langmuir* **21**, 12213 (2005).
14. D. Schondelmaier, S. Cramm, R. Klingeler, J. Morenzin, C. Zilkens and W. Eberhardt, *Langmuir*

18, 6242 (2002).

15. E. Hosono, S. Fujihara, I. Honma and H. Zhou, *J. Am. Chem. Soc.* **127**, 13458 (2005).

16. N. Saleema and M. Farzaneh, *Appl. Surf. Sci.* **254**, 2690 (2008).

17. H. Liu, L. Feng, J. Zhai, L. Jiang and D. B. Zhu, *Langmuir* **20**, 5659 (2004).

18. F. Shi, Z. Q. Wang and X. Zhang, *Adv. Mater.* **17**, 1005 (2005).

19. A. Safaee, D. K. Sarkar and M. Farzaneh, *Appl. Surf. Sci.* **254**, 2493 (2008).

20. D. K. Sarkar and M. Farzaneh, *Appl. Surf. Sci.* **254**, 3758 (2008).

21. D. K. Sarkar, M. Farzaneh and R. W. Paynter, *Materials Letters* **62**, 1226 (2008).

22. A. Safaee, D. K. Sarkar andM. Farzaneh, in: *Contact Angle,Wettability and Adhesion*, K. L.Mittal

(Ed.), Vol. 5, pp. 287–293. VSP/Brill, Leiden (2008).

23. D. K. Sarkar and M. Farzaneh, in: *Contact Angle, Wettability and Adhesion*, K. L. Mittal (Ed.),

Vol. 5, pp. 271–278. VSP/Brill, Leiden (2008).

24. N. Saleema, D. K. Sarkar andM. Farzaneh, in: *Contact Angle,Wettability and Adhesion*, K. L. Mittal

(Ed.), Vol. 5, pp. 279–285. VSP/Brill, Leiden (2008).

25. X. Chen, L. Kong, D. Dong, G. Yang, L. Yu, J. Chen and P. Zhang, *Appl. Surf. Sci.* **255**, 4015

(2009).

26. X. Chen, L. Kong, D. Dong, G. Yang, L. Yu, J. Chen and P. Zhang, *J. Phys. Chem. C* **113**, 5396

(2009).

27. B. Qian and Z. Shen, *Langmuir* **21**, 9007 (2005).

28. I. A. Larmour, S. E. J. Bell and G. C. Saunders, *Angew. Chem. Int. Ed.* **46**, 1 (2007).

29. M. Callies, Y. Chen, F. Marty, A. Pépin and D. Quéré, *Microelectronic Eng.* **100**, 78 (2005).

30. JCPDS, Cu (01-085-1326).

31. JCPDS, Ag (03-065-8428).

32. JCPDS, Cu2O (01-077-0199), CuO (01-078-0428).

33. D. K. Sarkar, X. J. Zhou, A. Tannous and K. T. Leung, *J. Phys. Chem. B* **107**, 2879 (2003).

34. M. L. Miller and R. W. Linton, *Anal. Chem.* **57**, 2314 (1985).

35. H. Seyama and M. J. Soma, *Chem. Soc. Faraday Trans. I* **81**, 485 (1985).

36. J. A. Gardella, R. L. Chin, S. A. Ferguson and M. M. Farrow, *J. Electron. Spectrosc. Relat. Phenom.* **8**, 343 (1976).