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Analysis of roughness parameters to specify superhydrophobic antireflective boehmite films made by the sol–gel process

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Abstract

Superhydrophobic antireflective boehmite films with different topographies were made by the sol–gel process with variation of heat-treatment temperatures and film thicknesses. A set of roughness parameters was determined from atomic force microscope (AFM) to relate the superhydrophobic and antireflective properties to the surface topographies. The results demonstrate the power of the roughness parameters to identify such superhydrophobic antireflective films.

Keywords: Sol–gel process; Films; Surfaces; Functional applications; Roughness parameters

1. Introduction

The development of superhydrophobic surface with a water contact angle higher than 150° has drawn great interest in recent years.[1–4] On such a surface, various phenomena such as adherence of snow, oxidation and electrical conduction are expected to be inhibited.[5] Furthermore, such superhydrophobic property facilitates the removal of particulate depositions such as dust and results in purification of the surface through rain, fog or dew (Lotus Effect).[6] The use of detergents is not necessary for such a surface, and thus the surface is environmentally friendly. On the other hand, antireflective (AR) films have also raised great interest.[7–10] Up to now, AR films have been applied on the cover glass for solar cells, glazings, windshields of automobiles, optical instruments and so on.[7–10] Especially in solar cell collectors the reflection loss is the notable disadvantage that limits energy efficiency. It is also critical to have broadband antireflection, which can cover the visible light band to increase the energy efficiency. Although a multi-layer can be deposited to increase the bandwidth over which low reflection loss can be obtained, it normally adds some complexity to the producing process. Therefore, simple synthesis of broadband AR films is warmly welcomed. The normal way of producing broadband AR surfaces is to make porous films. The refractive index of materials is related to its density, therefore when lowering the density by introducing pores the refractive index is also lowered. However, the problem is that water vapor and dirt particles are absorbed into the pores to increase the refractive index and then lower the antireflection, which limits the lifetime of the AR films. The solution is to combine the superhydrophobic property with the antireflective property. Then the films are repellent to water and dirt particles in the environment, keeping the surface of the AR films clean and leading to good performance. Therefore it is beneficial and necessary to realize antireflective and superhydrophobic properties simultaneously to the same film, which could be called a multifunctional film.

To produce a superhydrophobic surface, a rough surface is required together with a low surface energy. With a flat, hydrophobic surface it is possible to achieve a maximum contact angle for water of roughly 120°. However, by lowering the surface energy of the rough surface with a (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxysilane (denoted as FAS) top

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layer, a superhydrophobic (contact angle for water >150°) can be achieved.[5] To produce a broadband antireflective surface, a porous film is a solution. Therefore by making suitable surface roughness covered by a top FAS layer, superhydrophobic and antireflective properties can be realized simultaneously. Two common models are normally used to describe the wetting of rough or patterned surfaces. In the Wenzel model,[11] the liquid is assumed to completely wet the grooves of a rough surface. The apparent contact angle θ_A is then given by

$$\cos\theta_A = r\cos\theta_Y \tag{1}$$

where r is the ratio of the actual area of a rough surface to the geometric projected two-dimensional area, and θ_Y is the Young contact angle for a flat surface. The equation thus states that a rough hydrophilic surface ($\theta_Y < 90°$) should be more hydrophilic, and a rough hydrophobic surface ($\theta_Y > 90°$) more hydrophobic than a flat surface with the same chemical composition. If air is assumed to be trapped in the voids of a rough hydrophobic surface, the wetting can be described by the Cassie–Baxter equation:[12]

$$\cos\theta_A = f_1\cos\theta_1 - f_2 \tag{2}$$

where f_1 is the fraction of solid material in contact with the liquid, θ_1 the contact angle of pure solid material, and f_2 the fraction of air in contact with the liquid ($f_1 + f_2 = 1$).

The sol–gel process is a versatile method to prepare oxide-based films on a variety of substrates in an economical way.[13] The process is cost effective with easy operation. To characterize the surface roughness, atomic force microscopy (AFM) is a common method and the roughness parameters obtained from AFM can be utilized to analyze the surface properties. There is a long history in relating the wetting behavior (including superhydrophobic property) to the surface roughness,[12] however to the authors' knowledge it is quite rare to relate antireflective property to roughness parameters. In this paper, superhydrophobic antireflective boehmite (AlOOH) films were made with different optical transmittances by varying the heat-treatment temperatures and the film thicknesses. A set of roughness parameters was determined to characterize the superhydrophobic property and the antireflective property. The aim is not only to identify the superhydrophobic property but also to specify the antireflective property by the roughness parameters.

2. Experimental

2.1. Preparation of the sol–gel samples

The superhydrophobic antireflective boehmite films were made from aluminum tri-sec-butoxide (denoted as Al(O-sec-Bu)$_3$, $C_{12}H_{27}AlO_3$ > 97%, VWR), isopropyl alcohol (denoted as i-PrOH, C_3H_7OH > 99%, VWR), ethyl acetoacetate (denoted as EAcAc, $C_6H_{10}O_3$ > 98%, VWR) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trimethoxy-silane ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, denoted as FAS, ABCR GmbH & Co. KG, Karlsruhe, Germany). By varying the heat-treatment temperatures and the film thicknesses the superhydrophobic and antireflective properties can be tuned. In the experiments, two different sols (sol A and sol B) were prepared. In sol A, 3 g Al(O-sec-Bu)$_3$ and 50 ml i-PrOH were mixed and in sol B 3 g Al(O-sec-Bu)$_3$ and 30 ml i-PrOH were used. After mixing them for 1 h, 2 ml EAcAc was introduced, and then the solution was stirred for 1 h. After that, the mixture of 1 ml water and 5 ml i-PrOH was added for hydrolysis and with mixing for another 2 h the solution was ready for spin coating. The substrates in this work were microscope glass slides, which were firstly cleaned in acetone and then in ethanol ultrasonically for 10 min, and finally rinsed with distilled water. The specimens marked as A1-100, A1-300 and A1-500 were made from sol A by spin coating at 1500 rpm for 20 s. The samples were dried at room temperature under ambient condition for a few minutes, and then heat-treated at 100, 300 and 500 °C as denoted in the code in air for 15 min with a heating and cooling rate of 30 °C/min. After cooling down, the films were immersed into boiling water for 10 min, and then dried at room temperature under ambient condition. By using the same heat-treatment temperature of 300 °C, B1-300 and B2-300 were made from sol B with different amount of gel layers (1 and 2 layers) as indicated in the sample names. In B2-300, after depositing the first gel layer, heat-treatment at 400 °C for 30 min was carried out. Then a second gel layer was made. After that, heat-treatment at 300 °C and boiling water treatment were done. All the film samples were spin-coated only on one side. The surface chemistry of the as-synthesized films was finally modified by FAS. The FAS solution was prepared by mixing 1 ml FAS and 50 ml ethanol for 1 h. Then the film was immersed into the FAS solution for 1 h, followed by heating at 180 °C for 1 h. To measure the thickness of the FAS layer, the FAS layer was also made on the top of the bare glass by the same process.

2.2. Contact angle, film thickness and optical transmittance measurements

Water contact angles were measured by a system (Pisara, FotoComp Oy, Jyväskylä, Finland), which was composed of a microliter syringe for releasing the water droplet and an optical system connected to a computer for data analysis. The size of the water droplet was 5 μl for the measurement. Droplets were placed at five positions and the average value was accepted as the final contact angle value. Thickness of the boehmite films was measured with a field emission scanning electron microscope (FESEM, Hitachi S-4800, Japan). A thin layer of Pt/Pd was coated on specimens to improve conduction and image quality. Thickness of the FAS layer was examined by Optical Profilometer (Wyko NT1100, Veeco, USA). Optical transmittance of these films was measured with a UV–vis spectrophotometer (Shimadzu UV-2501PC, Japan).

2.3. AFM measurements and roughness parameters

Surface topography of the films was observed by atomic force microscope (AFM, Nanoscope IIIa, Digital Instruments, Santa Barbara, CA). All the images were recorded in tapping mode using silicon cantilevers with a resonance frequency between 250 and 300 kHz. All the images (512 × 512 pixels) were measured in air without filtering. The scanning probe image processor software (SPIP, Image Metrology, Denmark) was used for the roughness analysis of the images.[14]

A set of roughness parameters has been developed and standardized for versatile characterization of various surface properties.[15] The root mean square (RMS) roughness S_q is the most widely used amplitude roughness parameter that gives the standard deviation of height. Surface skewness S_{sk} describes the asymmetry of the height distribution. A skewness value equal to zero represents a Gaussian-like surface. Negative values of S_{sk} refer to a surface-porous sample, that is, the valleys dominate over the peak regimes. Respectively, the local summits dominate over the valleys when $S_{sk} > 0$. Two hybrid parameters have been developed to especially describe the form of the summits: the mean summit curvature, S_{sc}, and the RMS value of the surface slope, S_{dq}. Most of the above parameters contribute to the actual surface area: the absolute height difference, the number and form of local maxima, among others. A measure for the increase in actual surface area with respect to the projected two-dimensional area is given in percent by the surface area ratio parameter S_{dr}. A more thorough description of the roughness parameters can be found elsewhere.[16]

3. Results and discussion

The superhydrophobic antireflective boehmite films with different topographies were made by varying the heat-treatment temperatures and the film thicknesses. With different topographies the films show different optical transmittances and contact angles. Fig. 1 gives the optical transmittance spectra of A1-100, A1-300 and A1-500, in which optical transmittance of the reference glass substrate is also given. The optical transmittances of all the three films are better than that of the reference glass. Sample A1-100 has the smallest increment in optical transmittance and sample A1-300 has the highest. The high optical transmittance is over a broad bandwidth from 350 to 900 nm, which could be called broadband antireflective property. On the other hand, the contact angles for water of A1-100, A1-300 and A1-500 are 103°, 152° and 152° (Θ_m in Table 1). When the contact angle is above 90° the surface is hydrophobic and when the contact angle is more than 150° the surface could be called superhydrophobic. Typical AFM images of A1-100, A1-300, A1-500 and the shape of the water droplets on the surfaces are shown in Fig. 2. The roughness parameters of the three films are given in Table 1. The measured thickness of the FAS layer is 7 nm. Therefore the FAS layer modifies the surface energy while following the surface topography of the as-prepared boehmite films. The gel layer made from sol A is about 210 nm. After the heat-treatments at different temperatures and the boiling water treatment, the thickness of the films is also shown in Table 1. The increment in effective surface area S_{dr} is significant for A1-300 and A1-500 as compared to A1-100. This is the reason of the superhydrophobic behavior of A1-300 and A1-500. Air can be entrapped in the voids, which leads to a decrease in contact area between the water droplet and the surface, i.e. the droplet is in the Cassie–Baxter mode (Eq. (2)). The water contact angle of 103° on sample A1-100 indicates that the droplet on this surface is more in the Wenzel state (Eq. (1)), i.e. the liquid fills the grooves. Also the higher RMS-values of the surface slope, S_{dq}, and the mean summit curvature S_{sc}, of A1-300, A1-500 indicate the surface with sharp peaks. This means that the contact area between the water droplet and the surface is very small, and that the proportion of air below the droplet is large (larger f_2 value in Eq. (2)).

It seems that there is also good correspondence between the optical transmittance and the roughness parameters. A1-300, which gives the best optical transmittance, has the highest root mean square roughness value S_q while A1-100, which gives the least increment in optical transmittance, has the lowest S_q. And the optical transmittance and S_q of A1-500 are both in between. The skewness value S_{sk} describes the asymmetry of the height distribution. A1-300, with the smallest S_{sk} value, can be described as the sample least dominated by surface summits (peaks), which seems to give the best optical transmittance. On the other hand, A1-100 with the highest S_{sk} value gives the lowest increment in optical transmittance. The optical transmittance seems also to correlate with the hybrid parameters S_{sc} and S_{dq}. The higher values of S_{sc} and S_{dq} seem to give better transmittance. The differences of S_{sc} and S_{dq} between samples A1-300 and A1-500, however, are fairly small, too small to unambigu-

Table 1
Roughness parameters, measured water contact angles and film thicknesses of the film samples A1-100, A1-300 and A1-500

	A1-100	A1-300	A1-500
Thickness (nm)	100	170	170
S_q (nm)	2.7	28.1	16.0
S_{dr} (%)	2.5	71.7	46.1
S_{sk}	0.52	0.07	0.28
S_{sc} (1/nm)	4.7×10^{-4}	3.9×10^{-3}	2.7×10^{-3}
S_{dq} (1/nm)	0.2	1.3	1.1
Θ_m (°)	103	152	152

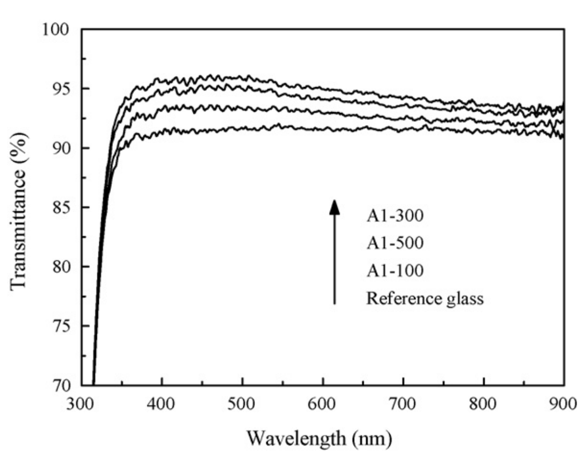

Fig. 1. Optical transmittance spectra of the reference glass substrate, and of the film samples A1-100, A1-500 and A1-300 (from down to up). The roughness values of the samples A1-500, A1-300 and A1-100 are found in Table 1.

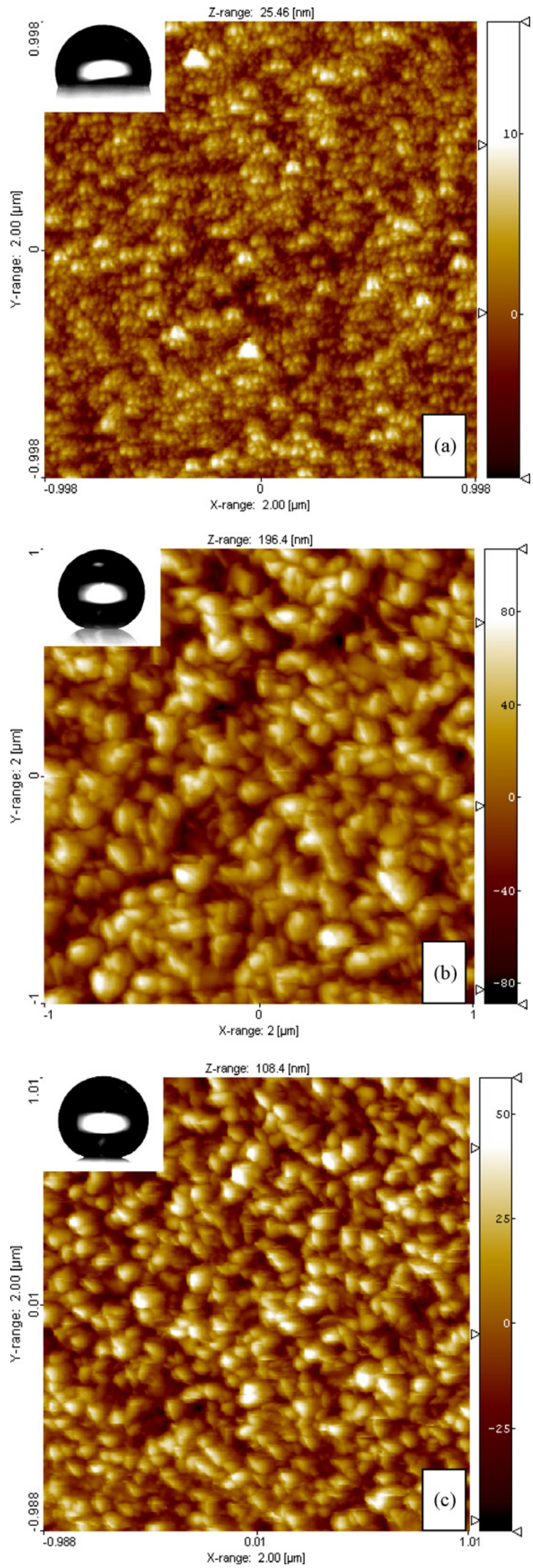

Fig. 2. AFM images (2 µm × 2 µm) of the samples: (a) A1-100 with z-range 25 nm, (b) A1-300 with z-range 196 nm and (c) A1-500 with z-range 108 nm.

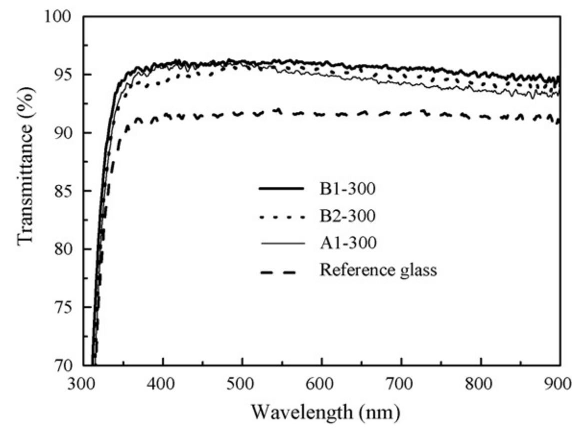

Fig. 3. Optical transmittance spectra of the reference glass, and of the film samples A1-300, B1-300 and B2-300.

ously explain the differences in optical characteristics between these two samples.

When varying the film thicknesses, optical transmittances are also different as shown in Fig. 3. However, all three films are superhydrophobic with contact angles for water above 150°. Fig. 4 gives typical cross-sectional FESEM images of the films A1-300, B1-300 and B2-300. The gel layer made from sol B is about 230 nm. In B2-300, after depositing the first gel layer, heat-treatment at 400 °C for 30 min was carried out. Then a second gel layer was made and the total film thickness is about 310 nm. After the heat-treatments at 300 °C and the boiling water treatment, the film thickness of A1-300 is about 170 nm, of B1-300 about 230 nm and of B2-300 about 320 nm. For A1-300 in Fig. 4(a), a thin layer of Pt/Pd had to be coated in the imaging process which makes the glass substrate look different with those in Fig. 4(b) and (c). The pores in A1-300 and B1-300 are open down to the glass substrate, while in B2-300 there is a more dense layer between the porous surface layer and the glass substrate. However, the structure difference does not affect the contact angle values. All films exhibit a sufficient roughness for a Cassie–Baxter state to be present.

However, the optical transmittances of these three film samples are different. When the wavelength is below 520 nm, A1-300 has a slightly better optical transmittance than B2-300. When the wavelength is above 520 nm, B2-300 has a slightly higher optical transmittance than A1-300. However, B1-300 has the best optical transmittance between 95 and 96% over the whole wavelength range. Furthermore, the cutting edge of the optical transmittance spectrum of B1-300 is lower than that of B2-300 and A1-300. Therefore B1-300 broadens the wavelength range with higher optical transmittance than the other two film samples, which increases the efficiency of such AR films. As shown in Table 2, B1-300 is the only film with a negative S_{sk} skewness value, which indicates that the surface becomes slightly dominated by valleys. For both A1-300 and B2-300 the skewness values are positive, i.e. the surfaces are dominated by peaks rather than valleys. The differences in skewness values seem at least partly to explain the optical behavior of the samples—sample B1-300, the only sample with negative skew-

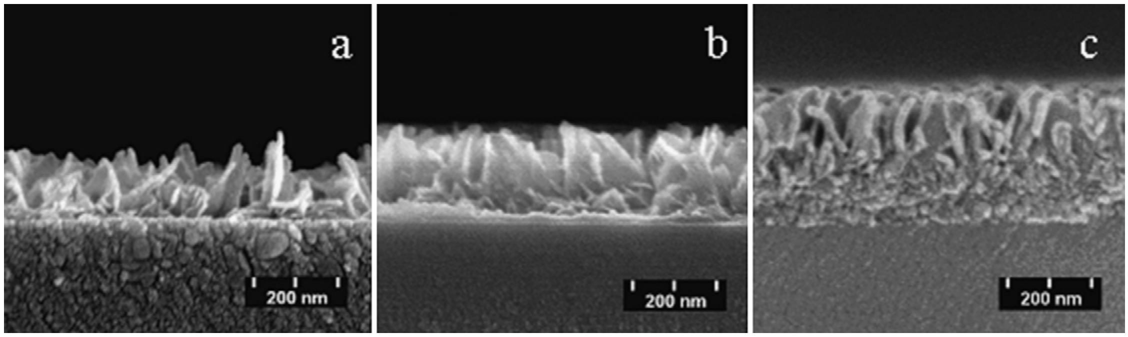

Fig. 4. Cross-sectional FESEM images of the film samples: (a) A1-300, (b) B1-300 and (c) B2-300.

Table 2
Roughness parameters, measured water contact angles and film thicknesses of the film samples A1-300, B1-300 and B2-300

	A1-300	B1-300	B2-300
Thickness (nm)	170	230	320
S_q (nm)	28.1	27.6	13.8
S_{dr} (%)	71.7	97.8	24.2
S_{sk}	0.07	−0.12	0.13
S_{sc} (1/nm)	3.9×10^{-3}	6.3×10^{-3}	2.6×10^{-3}
S_{dq} (1/nm)	1.3	1.6	0.7
Θ_m (°)	152	154	154

ness value, shows the best optical transmittance. The S_q values of A1-300 and B1-300, and the S_{sc} and S_{dq} values of all three films are quite close. Although it seems that higher S_q, S_{sc} and S_{dq} values relate to higher optical transmittance, it is difficult to draw unambiguous conclusions.

4. Conclusions

The superhydrophobic antireflective boehmite films were made by the sol–gel process. By varying the heat-treatment temperatures and the film thicknesses different optical transmittances and contact angles for water were obtained based on different topographies. According to the roughness parameters obtained from AFM measurements, the superhydrophobic property can be related to high S_{dr} value and the antireflective property to low S_{sk} value (preferentially negative value) and perhaps also high S_q, S_{sc}, S_{dq} values.

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