Superhydrophobic ZnO nanotowers

N. Saleema[*], D. K. Sarkar[*], M. Farzaneh[*] and E. Sacher[**]

[*] Canada Research Chair on Atmospheric Icing Engineering of Power Networks and Industrial Chair on Atmospheric Icing of Power Network Equipment, Université du Québec à Chicoutimi, Canada G7H 2B1
[**] Regroupement Québécois de Matériaux de Pointe, Department of Engineering Physics, École Polytechnique, C.P. 6079, Montreal, Québec., Canada H3C 3A7

ABSTRACT

Superhydrophobic zinc oxide (ZnO) nanotowers have been grown successfully on sodalime glass substrates by chemical bath deposition (CBD). Chemically and ultrasonically cleaned glass substrates have been immersed in beakers containing 100 ml of $0.1\,M\ Zn(NO_3)_2 \cdot 6H_2O$ and different amounts (4 – 10 ml) of 28% NH_4OH solution. The CBD has been performed in an oven at 70 °C for 18 hours. Surface morphology of the grown ZnO films have been carried out using field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). FESEM images have revealed the presence of randomly oriented hexagonal patterned ZnO nanotowers. The heights of the nanotowers are approximately 700 nm. Throughout 300 nm from the top of the nanotowers, uniform nanosteps with a step-size of 25 nm, both horizontally and vertically are observed, which is complementary with the AFM studies. These ZnO nanotowers have been passivated using stearic acid (SA) molecules for hydrophobic applications. Water contact angle of greater than 170° has been achieved after SA passivation with a contact angle hysteresis of less than 5°. The superhydrophobicity of these nanotowers is due to the coexistence of the nanosteps which effectively increases the surface area and present high contact angle.

Keywords: superhydrophobic, zinc oxide nanotower, chemical bath deposition, contact angle

1 INTRODUCTION

Superhydrophobic nanostructured thin films can be of great interest in many applications such as coating glass windows, camera lens, high-tension lines, etc. Commonly known examples that exhibit such a high contact angle of water are naturally existing tissues such as lotus leaves and Lepidoptera wings where the water droplet can freely roll off the surface without leaving any trace of beads [1]. Recent studies indicate that a two-tier roughness on a surface composed of micro- and nano-structure is essential to achieve such a superhydrophobicity [2, 3]. The Wenzel [4] and Cassie [5] model are the two existing resources that explain the impact of surface roughness on wettability.

Zinc oxide (ZnO) is widely used in diverse range of technological applications such as solar cells, photo detectors, light emitting devices, gas sensor elements, and surface acoustic wave guides due its unique structural, optical and electrical properties [6-10]. There exist several sophisticated techniques to synthesize ZnO thin films such as sputtering, pulsed laser deposition, chemical vapor deposition, molecular beam epitaxy, sol–gel process, etc. for different applications [11-15]. The chemical bath deposition (CBD), among various techniques, has gained popularity recently because it is simple, low cost and can be performed at low temperatures [16, 17]. The superhydrophobicity of such ZnO surfaces was achieved by passivating them using fluoroalkylsilane (FAS) [18]. Usually $-CF_3$ terminated surfaces such as FAS exhibit a water contact angle (CA) of more than 90° on a plane surface.

In this paper, we demonstrate the efficiency of the novel CBD technique performed at a temperature as low as 70 °C using a less complex aqueous solution, which results in a nanostructured surface consisting of several nanotowers decorated with nearly uniform nanosteps combined giving a binary structure. Superhydrophobic property of these ZnO nanotowers will be studied by passivating them using $-CH_3$ terminated organic molecules, which has a water CA of only 70° on a plane surface. We show in this study that with the smartness of our ZnO nanotowers, it is possible to achieve a very high superhydrophobicity even using an organic molecule which has such a low CA as compared to FAS.

2 EXPERIMENT

The CBD was performed in an oven at 70 °C for 18 hours in a beaker containing an aqueous solution as a chemical bath. The aqueous solution used for the chemical bath comprising of 100 ml of $0.1\,M\ Zn(NO_3)_2 \cdot 6H_2O$ and different amounts (4, 5, 6, 7, 8 and 10 ml) of 28% NH_4OH solution were contained in 6 different beakers. Soda lime glass substrates were ultrasonically cleaned with $0.1\,M\ NaOH$ for 10 minutes at a solution temperature of 35 °C, followed by water cleaning twice under the same ultrasonic conditions. After drying with clean air, the substrates were immersed in the beakers containing the chemical bath for coating. The coated samples were rinsed in a beaker containing methanol to remove any lose particles and were dried in an oven at 70 °C for several hours. They were then passivated using Stearic acid (SA) organic molecules prepared by dissolving $2 \times 10^{-3}\,mM$ SA in acetone for superhydrophobicity. The microstructural studies of these films were studied by LEO field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) (Nanoscope IIIa by Digital Instrument). The superhydrophobicity of these films were tested and measured using contact angle (CA) measurement equipment (Krüss GmbH, Germany).

3 RESULTS AND DISCUSSIONS

The growth process of ZnO nanotowers involves a chemical reaction during which the zinc nitrate decomposes to give ZnO in the presence of ammonium hydroxide, as follows [19].

$$Zn(NO_3)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4NO_3$$

$$Zn(OH)_2 + 2NH_4OH \rightarrow (NH_4)ZnO_2^- + H_2O + H^+$$

$$(NH_4)ZnO_2^- + H^+ \rightarrow ZnO + NH_4OH$$

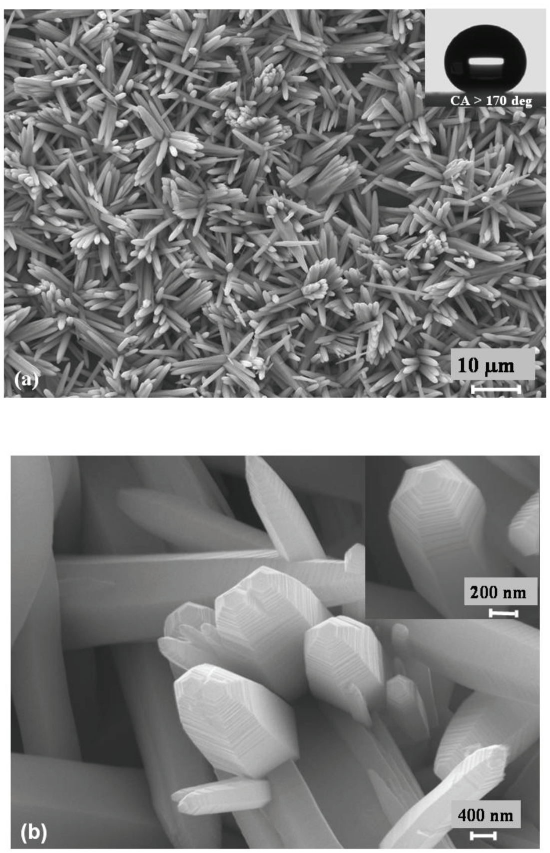

Figure 1. FESEM images of ZnO nanotowers at (a) low magnification; inset shows the image of a water drop (b) ZnO nanotowers at high magnification; inset shows a single nanotower to visualize the nanosteps.

Figure 1. shows the FESEM images of the ZnO nanotowers deposited on soda lime glass substrates by immersing them in beakers containing 100 ml of $0.1\,M\ Zn(NO_3)_2 \cdot 6H_2O$ and 7 ml of 28% NH_4OH solution. Figure 1 (a) shows the presence of randomly oriented hexagonal patterned ZnO nanotowers. The hexagonal patterns are very distinct as shown in Figure 1 (b). Figure 1 (b) and its inset clearly shows that the heights of these nanotowers are approximately 700 nm, the top 300 nm of which consists of uniform nanosteps with a step-size of 25 nm, both horizontally and vertically.

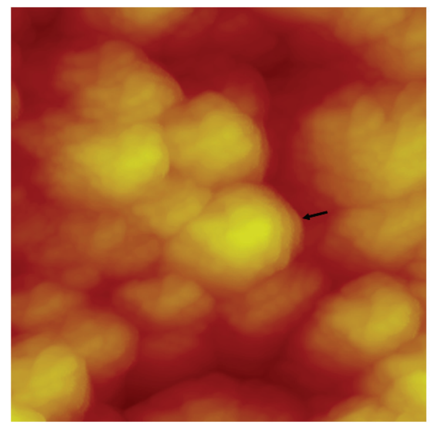

Figure 2. 2-D view of tapping mode AFM images of ZnO nanotowers grown on silicon substrate with a scan size 2 µm × 2 µm and data scale 300 nm; arrow shows a hexagon shaped nanotower

Figure 2 shows the AFM image of ZnO nanoparticles grown on silicon substrates for 20 minutes under the same experimental conditions as used on glass substrates, as it was difficult to perform AFM investigations for nanotowers shown in Figure 1 due to their high roughness. The presence of hexagonal nanotowers is also evident from the AFM image of the silicon grown ZnO sample which also showed a high superhydrophobicity on passivation in similar manner. The arrow in Figure 2 shows one of the corners of the hexagon. The presence of nanosteps can also be seen just above the arrow. The cross-section of one of the hexagons shows that the horizontal and vertical distance between the steps is around 25 nm and 30 nm respectively, which is very complimentary with the FESEM investigation of the inset of Figure 1 (b). The size of these nanoparticles, as observed in AFM, is ~300 nm with *rms* roughness of 105 nm. The dimensions of the nanotowers in Figure 1 (b) and Figure 2 of course vary as they were prepared differently. The AFM and SEM images clearly confirm the presence of a dual structure (presence of several nanosteps in each nanotower) that is similar to the micro-nanostructure present in lotus leaves.

These ZnO nanotowers were passivated using stearic acid molecules $(CH_3(CH_2)_{16}COOH)$ and tested for hydrophobicity. The $-CH_3$ head of SA is hydrophobic and

$-COOH$ tail is hydrophilic. The hydrophilic tail reacts with ZnO during passivation and keeps the hydrophobic head up. After passivation, the achieved values of the static CA of water is >170^o with a contact angle hysteresis (CAH) of less than even 5^o, rolling the water off from the surface. The CA of smooth silicon or glass passivated with SA is 70^o as we observed. Mei Li et al [18] have reported a CA of only >152^o for $-CF_3$ terminated ZnO films passivated using Fluoroalkylsilane (FAS). However, $-CF_3$ terminated surfaces have much lower surface energy than $-CH_3$ terminated surfaces and must give higher CA on a surface similar to our ZnO films. To understand the area fraction of water drop in contact with surface in our case and in the case of Mei et al [18], we have used the Cassie equation [5], which is written as

$$\cos\theta_c = f_1\cos\theta_1 + f_2\cos\theta_2 \quad (1)$$

where θ_c is the CA of the composite coating consisting of two components with contact angles θ_1 and θ_2 and corresponding area fractions f_1 and f_2. In such a composite system, if f_1 is assumed to be the material and f_2 is assumed to be air, eqn. (1) can be further modified as

$$\cos\theta_c = f_1(\cos\theta_1 + 1) - 1 \quad (2)$$

Hence, for SA passivated ZnO nanotowers (composite of ZnO and air) with θ_1 70^o and θ_c 170^o, the calculated f_1 is ~0.01. However, in Mei Li's case [18], when θ_c is 150^o and θ_1 110^o (CA of FAS [20]) f_1 is 0.20, which is ~20 times higher than our ZnO film. Due to this difference in the area fraction, we have obtained a superhydrophobic film with higher CA even using an organic molecule that exhibits a contact angle of less than 90^o. These differences are due to the well ordered nanosteps present in our ZnO nanotowers which effectively reduces the contact area of water.

Figure 3 shows the contact angle hysteresis (CAH) as compared to the static CA of water studied for ZnO nanotower films made using different amounts of NH_4OH. The inset of Figure 3 shows that the CA remains nearly constant up to 8 ml of NH_4OH and then starts reducing. It is clear from these graphs that after an addition of 8 ml of NH_4OH, an increase in CAH is observed with a decreasing CA. It was in fact impossible to measure the hysteresis for the films prepared with 10 ml NH_4OH in the solution, whereas the CA was still greater than 120^o. After this critical volume of NH_4OH (8 ml), further addition of more NH_4OH probably starts slowing down the growth process due to its etching property which reduces the dimensions of the nanotowers. This may create large gaps between the nanotowers, increasing the total water contact area, thus reducing the amount of air trapped in the gap. This still provides a CA >90^o, but according to Wenzel theory, we must expect a CA <90^o. Hence, even after this critical point, the system still behaves like the Cassie model, exhibiting a CA >90^o and we may call this behavior a 'sticky Cassie model'.

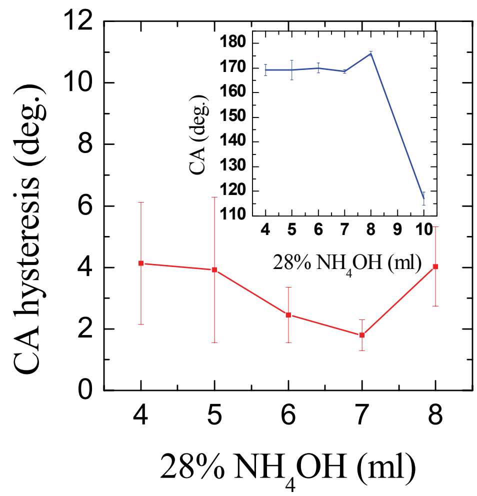

Figure 3. Contact angle hysteresis vs. amount of NH_4OH used in the solution to produce ZnO nanotowers; inset shows the contact angle plot vs. amount of NH_4OH.

4 CONCLUSION

Superhydrophobic ZnO nanotowers consisting of several nanosteps have been successfully grown on soda lime glass substrates by chemical bath deposition technique. These nanotowers are of approximately 700 nm high with nanosteps of approximately 25 nm throughout the top 300 nm of the nanotowers. After stearic acid passivation of these surfaces, a very high water contact angle of higher than 170^o has been achieved with a hysteresis of lower than 5^o when less than 8 ml of NH_4OH was used with the aqueous solution. The addition of more NH_4OH only increases the contact angle hysteresis and starts sticking to the surface.

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