NANOSTRUCTURED SUPERHYDROPHOBIC ZnO SURFACE LAYER ON Al-SUBSTRATE

Debasis De[1,2], D. K. Sarkar[1] and D. Kocaefe[1]

[1]Centre Universitaire de Recherche sur l'Aluminium (CURAL), L'Université du Québec à Chicoutimi, 555 Boulevard de l'Université, Chicoutimi, Québec, Canada G7H 2B1.
[2]Electronics and Instrumentation Engineering Department, Dr. B.C. Roy Engineering College, Durgapur, West Bengal-713206, India.

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Abstract

Nanostructured superhydrophobic ZnO films have been fabricated on aluminum surface by a simple and cost effective chemical bath deposition technique. A perfectly hexagonal shape of ZnO nanoplates is clearly observed in the scanning electron microscopic images. The average size of these unique hexagonal plates is ~ 4 µm side and ~ 30 nm of thickness. The tendency to form hexagonal morphological features is due to the hexagonal crystal structure of the ZnO. On stearic acid passivated ZnO surface, the superhydrophobicity is achieved by observing water contact angle of greater than 160° with a contact angle hysteresis of less than 5°. The superhydrophobicity of nanostructured ZnO film is observed due to high surface roughness and low surface energy.

Introduction

After a rainfall, shining of nearly spherical water drops on certain leaves is one of the most beautiful wonders of nature. Such natural phenomenon is observed not only on plants' leaves, but also on the body of several living creatures [1]. The water repellency phenomenon is well understood on lotus leaves and is called as 'lotus effect' [2]. This is considered as the basis of the studies of superhydrophobicity. The microscopic observation of the lotus leaves under scanning electron microscope show the coexistence of combined micro-nanostructured pattern which is again covered with a hydrophobic wax component. Two basic mathematical models, Wenzel [3] and Cassie and Baxter [4], are used to explain the contact angle behavior of rough surfaces. In general, a water droplet contact angle less than 90° indicates a hydrophilic surface while an angle greater than 90° present a hydrophobic one. If the water contact is higher than 150°, the surface called superhydrophobic, and on such a surface, water drops would roll off with nearly zero wetting which is also called self-cleaning surface. Study of the wetting properties of solids by liquids and interfacial phenomena are not only important in fundamental research but also significant technological issues. In many areas of technology it is required to control the wettability of surfaces. Self-cleaning property is desirable for car windshields, aircraft, solar energy cells, anti-sticking of snow on glass window [5], etc. Apart from these, superhydrophobic surfaces have several emerging applications in a large number of fields such as anticorrosive industrials parts, antibiofouling paints for boats, biomedical applications, microfluidics, textiles, current conduction, bio-chips and many others [6, 7].

Generally, superhydrophobic surfaces are prepared by combining two steps that involve the creation of a rough micro-nano patterning on surface in the first step and passivation of this rough surface using low surface energy coating in the second step. Various techniques have been developed to prepare rough surface patterns, and also to control the shapes, dimensions, and regularity of the surface, such as lithography, sol–gel, plasma etching, chemical etching, chemical bath deposition (CBD) technique, [8-10] etc. Song et al. [11] have been synthesized hexagonal, bullet-like ZnO microstructures and nanorod by a simple hydrothermal method without surfactants. Kuo et al. [12] studied on hydrothermal synthesis of ZnO microspheres and hexagonal microrods with sheetlike and slatelike Nanostructures. High crystalline ZnO with hexagonal dumbbell-like bipods morphology was successfully synthesized via N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB)-assisted hydrothermal microemulsion route [13]. In a recent study, Saleema et al. reported on superhydrophobic properties of aluminum surfaces by creating a certain nanoroughness using a chemical etching. They also studied superhydrophobic properties of ZnO coated Al substrate by sol-gel spin coating and they have achieved a contact angle greater than 160° on this surface. [14]. In another study, ZnO nanotowers coated silica substrate showed highly superhydrophobic with a contact angle ~ 173° [15]. Sarkar et al. [16] reported superhydrophobic properties of micro-nanorough aluminum substrates upon coatings with fluorinated hydrocarbon providing a water contact angle of 165° and contact angle hysteresis below 2°. In this article, we report on controlled synthesis of nanostructured ZnO by CBD technique and superhydrophobic properties of ZnO coated Al substrate.

Experimental procedure

Aluminum alloy coupons (AA6061) of rectangular shape were ultrasonically degreased in 1% Liquinox solution for 10 min. Then the coupons were washed by water followed by ultrasonication with acetone for 15 min. Finally, the coupons were washed with deionized water in ultrasonic bath for experimental used. Then, ultrasonically cleaned aluminum coupon has immersed in a chemical bath consisting of 40 ml of aqueous 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ and 2 ml of 28% aqueous NH_4OH solution for the growth of ZnO via CBD technique. The ZnO was grown on aluminum coupon at hot plate temperature of 75 °C. After coating the coupon was taken from the solution and ringed by deionized water. After that, the ZnO coated coupons were kept for drying at an oven temperature of 70 °C for more than 10 h. Finally, the coupons were passivated with 0.01 M stearic acid (SA) in ethanol for 15 min by immersion for further characterizations. The morphological and elemental analyses of the ZnO coated aluminum coupons were performed using a scanning electron microscope (SEM, JEOL JSM-6480 LV) equipped with energy dispersive X-ray spectroscopy (EDX). The X-ray diffraction (XRD) analyses of the samples were carried out using a Bruker D8 Discover system. The wetting characteristics of the samples surfaces were carried out using contact angle goniometer (Krüss GmbH, Germany). The advancing and receding contact angles were measured by fitting images of the asymmetric water drops using the tangent-2 method with Krüss DSA software. The difference between the advancing and receding contact angles is the contact angle hysteresis.

Results and discussion

Nanostructured ZnO can be synthesized by various techniques. Among them CBD technique is very simple and cost effective. Here, we use NH_4OH for the preparation of ZnO. When NH_4OH is firstly introduced into the solution, $Zn(OH)_2$ sediment is formed. By adding more amount of NH_4OH and agitating the solution for a few seconds, it become clear again, indicating that the Zn^{2+} ions had combined with NH^{4+} ions to form stable zinc ammine [17]. As compare to the other method, here ammonium hydroxide enables a buffering mechanism of slowly releasing

Zn^{2+} and results unique growth of ZnO in a unique hexagonal shape as discussed later. Some general chemical reactions involved in the solution are listed below to tune the growth process of ZnO [18]:

$$NH_4OH \leftrightarrow NH_4^+ + OH^- \quad (1)$$

$$NH_4OH \leftrightarrow NH_3 \uparrow + H_2O \quad (2)$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2 \quad (3)$$

$$Zn(OH)_2 + 4NH_4OH \leftrightarrow Zn(NH_3)_4^{2+} + 4H_2O + 2OH^- \quad (4)$$

$$Zn(OH)_2 \leftrightarrow ZnO + H_2O \quad (5)$$

All above reactions are collectively in dynamic equilibrium and by differing any one would change the synthesis outcome. By tuning the experimental parameters, morphology of ZnO can varied, which will effect on roughness of the surfaces.

Figure 1 shows the SEM images of thin plates of hexagonal ZnO. While Figure 1(a) shows randomly oriented perfectly hexagonal patterned ZnO nanoplates, the hexagonal plates have regular edges with an angle of 120° between adjacent sides. The tendency to form hexagonal morphological features is due to the hexagonal crystal structure of ZnO [19] confirmed from x-ray diffraction pattern. This structure is also confirmed in transmission electron microscopic images (Figure not shown). These nanoplates are oriented in both parallel and perpendicular directions to the aluminum surface. It is also observed from image that the plates are lying on so many nanoflakes which are perpendicular direction to the aluminum surface. To further examine the surface structure of these plates, a high-magnification SEM image of few plates was obtained and is shown in Figure 1(b). The top surface of the nanoplates is pretty smooth and the average size of these hexagonal plates is ~ 4 μm side and ~ 30 nm of thickness.

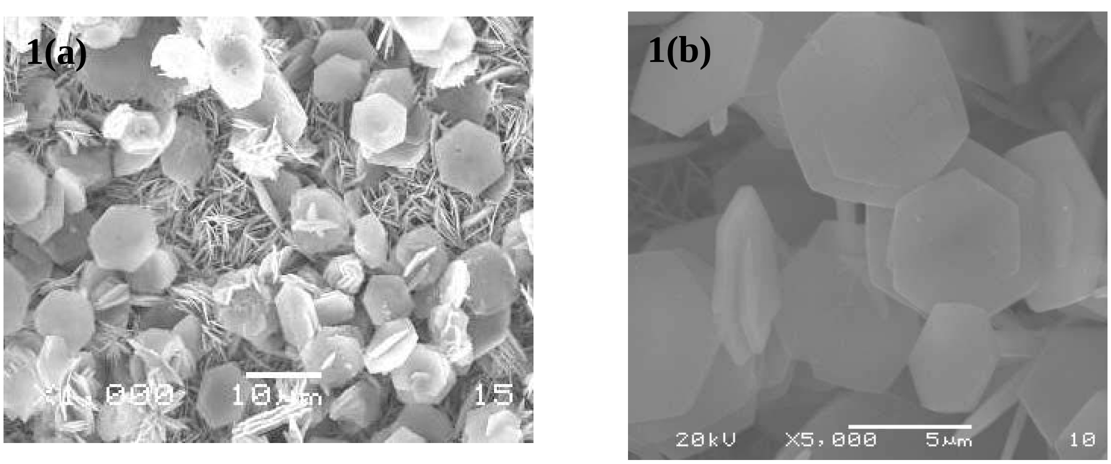

Figure 1. SEM images of ZnO nanoplates at (a) low magnification (b) ZnO nanoplates at high magnification showing perfectly hexagonal morphology.

To determine the composition of the sample, EDX spectra coupled to SEM and TEM are recorded. Fig. 2 presents typical EDX spectrum from SEM image shown in the inset. The spectrum confirms the presence of zinc and oxygen elements in the ZnO phase. A considerably large peak of aluminum element is observed due to the use of aluminum substrate.

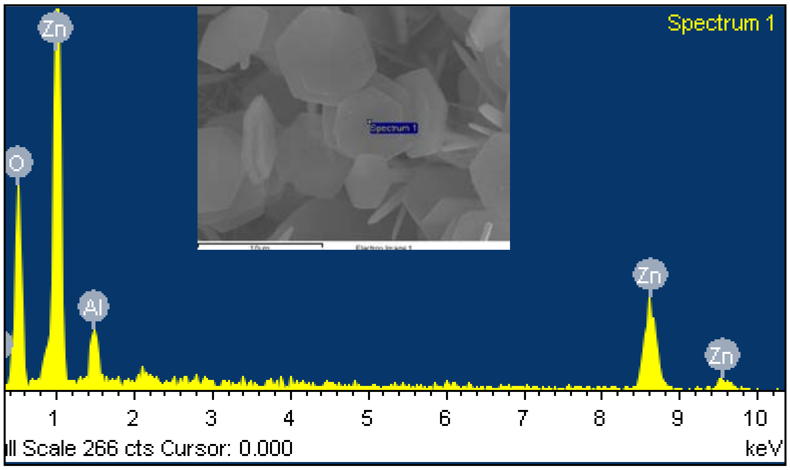

Figure 2. EDX spectrum of hexagonal ZnO nanoplates with the SEM image in the inset.

The ZnO coated on aluminum substrate dried in a closed and clean oven was found to completely absorb water. However, our hexagonal ZnO nanoplates become highly superhydrophobic, after passivation with SA, providing a contact angle (CA) as high as 164 ± 1.1° and a contact angle hysteresis (CAH) as low as 4 ± 0.5° (shown in Figure 3), water drops rolling off the surface with even the slightest tilt of the sample. Such a very low hysteresis of 4 ± 0.5° is comparable with very low hystereses of 1.4 ± 0.5° reported by Seleema et al. [15] on SA modified ZnO nanotowers on silicon substrate. Such a low hysteresis on the superhydrophobic ZnO surface is due to the presence of the binary structure composed of randomly oriented nanoplates, that eventually reduces the area of contact between the drop and the nanoplates and trapping more air [20, 21].

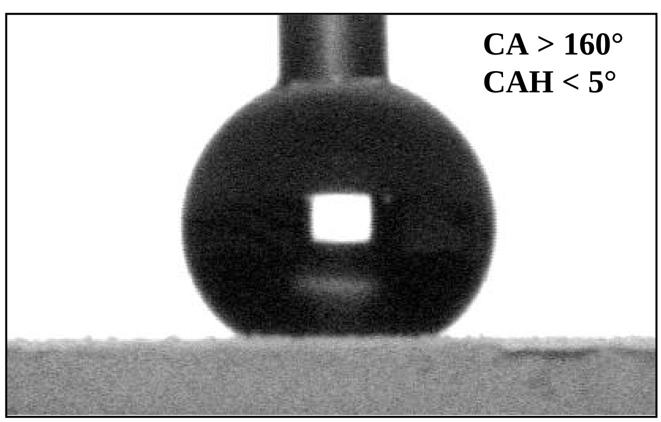

Figure 3. Image of a water drop on the surface of ZnO layer after SA passivation.

Conclusions

The nanostructured ZnO surface layer on aluminum substrate has been prepared by a simple chemical bath deposition technique. The average size of the as prepared hexagonal ZnO nanoplates is ~ 4 µm side and ~ 30 nm of thickness, which are oriented in both parallel and perpendicular directions to the Al-surface. Stearic acid passivated ZnO nanoplates provides a very high contact angle ~164 ± 1.1° with a low contact angle hysteresis ~ 4 ± 0.5°.

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