Applied Surface Science 264 (2013) 344–348

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Hydrophobic/hydrophilic switching on zinc oxide micro-textured surface

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ARTICLE INFO

Article history:
Received 25 July 2012
Received in revised form
24 September 2012
Accepted 4 October 2012
Available online 16 October 2012

Keywords:
Hydrophobic
Hydrophilic
Ultraviolet
Annealing
Zinc oxide
Microrod

ABSTRACT

Switchable wettability of zinc oxide (ZnO) microrod coated surfaces was controlled in two different ways: (1) by physical geometry (surface coverage area S_A: the area covered by solid) and (2) by irradiation with ultraviolet (UV) light followed by infrared (IR) or furnace heating. In the first approach, the threshold coverage area for achieving hydrophobic surfaces was found to be <40%, which is in good agreement with predicted values in the literature leading to a metastable *Cassie–Baxter* regime. The transformation of hydrophobic to hydrophilic surfaces was studied by alternating cycles of 3 h exposure to ultraviolet ($\lambda_{peak} \sim 253$ nm) light followed by 1 h of annealing or IR irradiation alone. Three different annealing temperatures (120 °C, 200 °C and 250 °C) were utilized. Results of this work can be applied for designing surfaces with controlled wettability.

1. Introduction

The wettability of a surface is influenced by its morphology (surface roughness, micro-nanostructure) and the material dependent surface energy [1–4]. However, hydrophilic (water contact angle, WCA < 90°) materials can be turned hydrophobic (WCA > 90°) and even superhydrophobic (WCA > 150°) by micro and nanostructuring the surfaces. The phenomenon of surface wettability is well understood and explained by *Wenzel* model [2] and the *Cassie–Baxter* model [5–8]. In the *Wenzel* model, it is presumed that all topographical features of the surface are completely wet by the applied liquid. In other words, the surface is completely saturated by the liquid since only solid and liquid interface are considered. In the *Cassie–Baxter* state [1], the applied liquid is considered to form an interface that lies on top of the topographical facets (e.g. touching only the tips of the structured surfaces) without penetration into the valleys whereby solid, liquid and air interfaces are considered in this regime, which is commonly referred to as the "*Fakir Effect*" [9]. Depending on the surface structure and material used for structuring, transitions between these two states are possible [7].

In 2008, theoretical studies of Duez et al. showed that a surface of parallel striped structures with lateral length scale from 1 to 10 μm and less than 40% solid fraction (60% was comprised of air) is hydrophobic [10]. Shastry et al. demonstrated that the height to pillar diameter (h/a) is an important factor for determining hydrophobicity [11]. We have previously reported that the surface hydrophobicity follows the pillar height when spacing between pillars is kept constant [12]. Das et al. have recently shown that WCA can be changed from 104° to 135° by the simple manipulation of surface morphology [13]. As early as 2007, Bhushan et al. proposed that the spacing factor, the ratio between diameter of pillar to the pitch distance, affects the hydrophobicity in the *Cassie–Baxter* regime [14]. A tailored superhydrophobic surface with dual roughness surface has also been reported by He et al. where unitary (single roughness surfaces) or dual roughness surfaces fabricated on silicon substrates resulted in WCA to abruptly change from 53° for unitary structures, to 156° in the case of binary structures [15]. Ning et al. reported on superhydrophobic surfaces fabricated on zinc substrate [16]. Hexagonal cavities covered with platinum nanoparticles of 50 nm (average diameter) led to the dual roughness structures which gave a WCA of 171°. Hou et al. applied a low surface energy material on ZnO microrods and reported a change in the wettability from a WCA of 40° to 153°, characteristic of a superhydrophobic surface [17].

Since the report of Sun et al. in 2001 on the photoinduced surface wettability conversion on ZnO and titanium dioxide (TiO_2) thin films, there has been much activity concerning the interaction of water droplets on nanostructured coatings formed by metal oxide particles consisting of nanorods and microrods [18].

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http://dx.doi.org/10.1016/j.apsusc.2012.10.024

Recently, Khranovskyy et al. reported photoinduced surface wettability on different ZnO nanostructures. It showed the effects of nanostructure size upon switching rate and wetting nature under UV illumination [19]. Switchable wettability of ZnO microrods was shown by Han and Gao in which WCA was varied from 0° to 151° under cycles of ultraviolet exposure and darkness [20]. In 2010, Lin et al. reported the controlled wettability of titanium oxide (TiO_x) surfaces using UV–vis (Ultraviolet–Visible) light irradiation [21]. In 2010, Lv et al. proposed the surface wettability switching on ZnO nanorods with different growth times. The proportion of nonpolar to polar surface was mainly attributed to the wettability switching in the longer growth of ZnO nanorods [22]. Lü et al. have proposed that the surface wetting transition from hydrophobic to superhydrophilic on the sodium (Na) doped ZnO thin film occur due to the presence of Na which creates more photo active sites on the surface that can be reversed by annealing over extended times in the ambient [23]. The mechanism of light-induced wettability changes in ZnO nanostructure has been reported by many groups [24–28].

We report here an experimental design to observe the effect of surface coverage of ZnO microrods on hydrophobicity, switching wettability (by applying UV/IR irradiation) of ZnO microrods array surfaces and optimization of the heating temperature for recovery to its original state (hydrophobic state). The purpose of using ZnO microrods was to develop a surface that reduces the contact area between solid and water (in this case solid, liquid and air regime) compared to a flat surface (solid and liquid only) that can be achieved by coating with ZnO nanocrystallites. We also compare results with our previous work [12] in which surfaces consisting of patterned microbumps showed superhydrophobic behavior with WCA exceeding 150° – a straightforward demonstration of the *Cassie–Baxter* case and surface behavior as hypothesized by Duez et al. [10].

2. Experimental

2.1. Chemicals

Analytical grade zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and sodium hydroxide (NaOH) (both from MERCK, Germany), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) (APS Ajax Finechem, Australia), hexamethylenetetramine ($((CH_2)_6N_4)$) (Aldrich, USA), and isopropanol ($((CH_3)_2CHOH)$) (Lab Scan, Ireland) were used without further purification. Standard microscope glass slides were used as substrates for zinc oxide microrod growth. The seeding process to grow ZnO microrods was accomplished by two methods described below.

2.1.1. Preparation of ZnO nanocrystallite for seeding process

Method 1: ZnO nanocrystallite seed stock was prepared by a hydrolytic procedure described in detail elsewhere [29]. Briefly, a solution of 20 mM sodium hydroxide in isopropanol was added drop by drop to 1 mM zinc acetate solution under continuous stirring. The mixture was hydrolyzed at 60°C for 2 h to form ZnO nanocrystallites. Nanocrystallites were then deposited dropwise (solution dropping method) on clean glass substrates kept constant at 60°C. Following the coating with ZnO crystallites, the substrates were annealed at 250 °C in air to remove any un-reacted chemicals on the surface.

Method 2: ZnO nanocrystallites were also formed by the decomposition of zinc acetate directly on glass substrates by thermal treatment in air. When the temperature of the glass substrate reached ca. 350 °C, zinc acetate decomposed into ZnO to form nanocrystallites. These nanocrystallites were used as seeds for the growth of ZnO microrods [30].

2.1.2. Hydrothermal growth of ZnO microrods

Following seeding on glass substrates (that are naturally hydrophilic), microrods were grown by a hydrothermal process in a chemical bath containing equimolar (20 mM) solutions of zinc nitrate hexahydrate and hexamethylenetetramine at 90 °C [30]. The hydrothermal growth process of ZnO micro and nanorods are well understood with several reviews available in the literature [31–34]. Depending upon the concentration of the reactants and the temperature of growth in the hydrothermal bath, the formation of regularly shaped rods with varying widths are observed [30]. The growth was carried out for 20 h with the precursor solution replaced every 5 h to replenish zinc ions [29]. ZnO microrod coated substrates were carefully rinsed several times with deionized (DI) water and annealed at 250 °C for 1 h to remove un-reacted organic matter. As-prepared samples were dried at 100 °C for a few hours prior to all measurements.

2.2. Water contact angle (WCA) measurements and surface area estimation

Water droplet of 5 μL was used for all WCA measurements. A minimum of five measurements for each surface on different portion of the substrates were conducted to provide a mean value. WCA was recorded with a customized contact angle instrument equipped with Dino Lite Pro AM 413T digital microscope camera. WCA values were determined and analyzed with *ImageJ Analysis* software following a method described by Stalder et al. [35]. The dimensions of ZnO microrod were estimated from scanning electron microscope (SEM) images. Coverage area (S_A) of ZnO microrods was also estimated from SEM images using the image analysis software.

The wettability conversion experiments were conducted using commercial UV lamp equipped with 6 W dual lamps yielding about 1.0 mW/cm^2 intensity. A standard furnace was used for heating. Both the experiments were conducted under ambient atmospheric (air) conditions with relative humidity (RH) ~ 65%.

3. Results and discussion

3.1. Wettability vs. surface morphology

In our laboratory findings, the WCA of a solid thin layer of ZnO formed by nanocrystallites deposited on glass substrates was found to be 26° ± 3° (this WCA is called intrinsic contact angle), which confirm that continuous, un-structured and untreated ZnO surfaces (so called flat surfaces) are hydrophilic in nature [12].

Fig. 1a shows scanning electron micrograph (SEM) image of ZnO microrods grown on a seeded glass substrate following *Method 1* [29]. The ZnO microrods were ca. 5.0 ± 0.5 μm in height with a width of 1.2 ± 0.1 μm as estimated from the cross section (not shown here) and top view of SEM images (Fig. 1a). The purpose of using 5.0 μm long ZnO rods is that hydrophobicity of unitary (single roughness) structured ZnO surfaces saturate for longer rod arrays [12]. Coverage area, the area covered by ZnO microrods (S_A) of samples was found to be less than 39% in these samples (Fig. 1a) which is also reported in our previous work [12]. On the other hand, the remaining area of 61% was air. However, the estimated S_A of the glass substrate covered with ZnO microrods was certainly overestimated because ZnO microrods were not all positioned normal to the surface. The static WCA was found to be ca. 123° ± 3° which is a demonstration of the formation of hydrophobic surface through the microstructuring of a native hydrophilic material (ZnO).

Fig. 1b represents a typical SEM image of ZnO microrods grown on seeded substrate synthesized following *Method 2*. On an average, the surface coverage was found to be higher than 60% (in the