

Tunable wettability in surface-modified ZnO-based hierarchical nanostructures

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Designing geometrical structures and making chemical modifications are two effective routes to tailor wettability. ZnO-based hierarchical nanostructures, in particular, vertically aligned nanoneedles and nanonails were employed as a platform to study the effect of surface morphology. The hydrophobicity and the variation of contact angle in the as-grown samples were attributed to the combined effects of surface roughness and partial water-solid contact. Subsequent chemical modifications with stearic acid led to superhydrophobic ZnO surfaces, while annealing in air resulted into superhydrophilicity. Under the alternations of coating and removal of stearic acid, reversible transitions between superhydrophilicity and hydrophobicity were realized. © 2008 American Institute of Physics. [DOI: 10.1063/1.2918447]

Wettability is a defining property of the interface between liquid and solid. Controlling surface wettability is of vital importance for a wide range of biological, chemical, and electronic applications.^{1,2} The wetting behaviors are mainly governed by two factors, surface geometrical structure and chemical composition.² Inspired by living organisms in nature,^{3,4} superhydrophilic surfaces with water contact angles (CAs) smaller than 5° and superhydrophobic surfaces with CA larger than 150° have been intensively pursued.^{5–11} Recently, there have been lots of interests in studying the wetting behaviors of nanomaterials based on ZnO, which is a technologically important wide-band-gap semiconductor with many promising properties.^{12–16} For nanoscale devices aimed for chemical and biological sensing,^{17–19} surface wettability plays a very important role. So far, most previous works have been focused on ZnO nanorods, nanowires, and nanobelts.^{12,14,19} There have been few studies on ZnO hierarchical nanostructures to explore in detail the geometrical effects of engineered surfaces.

In this work, we investigated vertically aligned Cu-doped ZnO hierarchical nanostructures with a smooth morphological transition between nanoneedles and nanonails to search for the optimized hydrophobic state. The unique self-assembly of these hierarchical structures with tunable complexity presents a convenient and effective means to adjust the surface wetting behaviors. Thermal annealing in air and surface modification with stearic acid were found to render the ZnO surfaces superhydrophilic and superhydrophobic, respectively. Reversible conversions between hydrophobicity and hydrophilicity were also observed.

Cu-doped ZnO nanostructures were synthesized using a facile vapor transport method with detailed conditions previously reported.²⁰ Briefly, Zn and CuCl₂ powders with a weight ratio of 5:1 were put in a quartz tube inside a horizontal furnace. After Au catalyst coating, a silicon substrate was placed on the right side and 2.5 cm away from the

source. For the growth, the tube was pumped down to 10⁻³ torr and the temperature reached 600 °C. Ar gas mixed with 5% oxygen was used to carry the vapor to the substrate. The growth of ZnO nanostructures usually lasted 15 min before the furnace was quickly cooled down to room temperature. The structural properties of the products were investigated by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM). As shown in Fig. 1(a), the XRD pattern corresponds to the wurtzite structure of ZnO with no detectable secondary phase. The redshift of the (002) peak [inset of Fig. 1(a)] after Cu doping can be

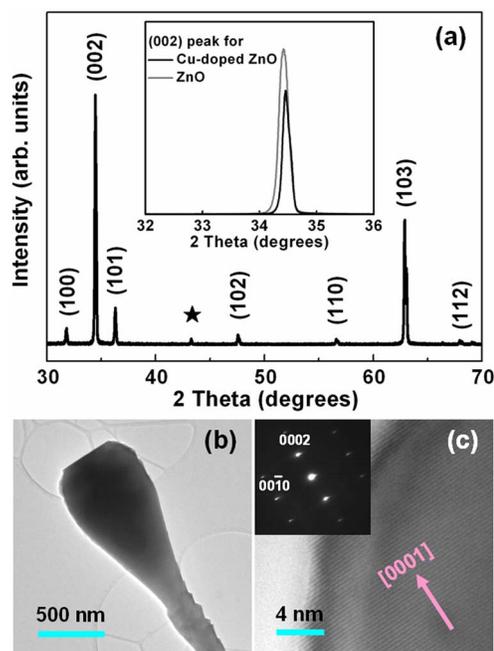


FIG. 1. (Color online) (a) XRD pattern of the Cu-doped ZnO sample. The star indicates a peak from the Au catalyst. The inset is the (002) peaks of the undoped and the Cu-doped samples. (b) Low-resolution and (c) high-resolution TEM images of a nanonail. The inset of (c) shows a SAED pattern.

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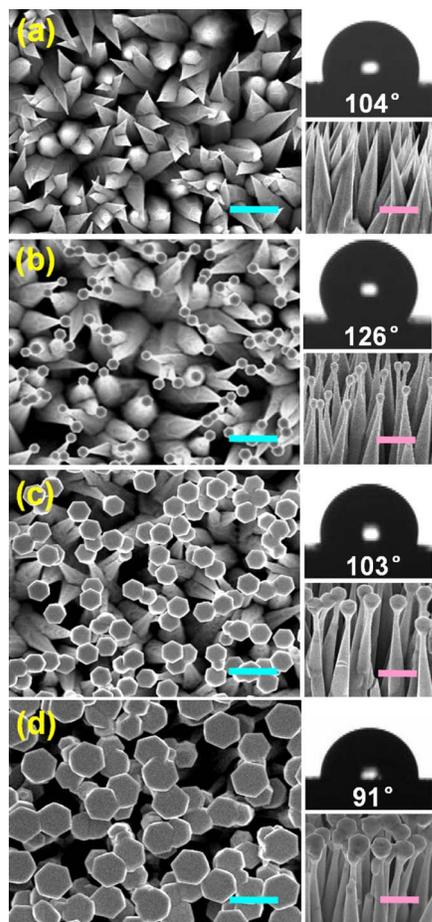


FIG. 2. (Color online) FESEM top and cross-section views of (a) nanoneedles and [(b–d)] nanonails of Cu-doped ZnO grown on silicon substrates. Photographs of water droplets and CA measured on each position are shown at the top right corners. The scale bars represent 5 μm in length.

attributed to the substitution of smaller Cu ions at the Zn sites. Preliminary chemical analysis showed that the Cu content in the final products is $\sim 0.3\%$. A typical TEM image was shown in Fig. 1(b). The high-resolution image in Fig. 1(c) indicates that the nanostructures grow along the [0001] direction. The selected area electron diffraction (SAED) pattern [inset of Fig. 1(c)] suggests a wurtzite structure, consistent with the XRD result.

One salient feature of the ZnO-based nanostructures is a gradual transition between different hierarchical morphologies, which allows us to investigate the geometrical effects on the wetting behaviors. The morphologies of as-grown samples were characterized by a field-emission scanning electron microscope (FESEM). Due to some subtle environmental changes at different locations on the growth substrate, Cu-doped ZnO nanostructures evolve from nanoneedles [the left end of the substrate, near the source, Fig. 2(a)] to nanonails [the middle and the right end of the substrate, Figs. 2(b)–2(d)]. With CuCl_2 in the source and careful control of the growth conditions, the synthesis of these hierarchical ZnO structures is highly reproducible. However, in order to understand the detailed experimental conditions and mechanisms responsible for the formations of these complex structures, further studies are required. As we will show, the surface structures and the chemical modifications determine the wettability of the ZnO surface. The Cu doping itself does not significantly affect the wetting behaviors.

The gradual morphological evolution introduces hierarchical structures composed of microscale and nanoscale features, which directly affects the surface wettability. The static water CAs were measured with a FTA1000 Drop Shape Instrument at room temperature. CAs measured at four evenly spaced positions on the substrate are shown in Figs. 2(a)–2(d). For each position, more than ten images were recorded. The typical error of the CA measurements is $\sim 3^\circ$. As depicted in the top and side views in Fig. 2(a), the base diameters of the nanoneedles are $\sim 5 \mu\text{m}$ and the tip dimensions are tens of nanometers. As the cap size of the nanonails monotonically increases, a modulation of the static CAs was observed. Starting with a CA of 104° for the nanoneedles [Fig. 2(a)], CA increases to 126° for nanonails with caps of $\sim 800 \text{ nm}$ [Fig. 2(b)], then decreases to 91° when the caps start to overlap [Fig. 2(d)]. The magnitude of CA modulation is 35° , larger than the previous results achieved in controlled ZnO surface structures.¹⁵

The observed trend of CA modulation is quite reproducible for several samples. As we will show later, it persists even after the samples were chemically modified. This tunable wetting behavior is closely related to the morphology of nanostructures. For a liquid drop on a solid surface, the Young CA θ is determined by the surface free energies involved²¹

$$\cos \theta = (\gamma_{sv} - \gamma_{sl}) / \gamma_{lv}, \quad (1)$$

where γ_{sv} , γ_{sl} , and γ_{lv} are the solid/vapor, solid/liquid, and liquid/vapor tensions, respectively. CA is usually modified for complex surfaces with hierarchical structures. The transition from nanoneedles [Fig. 2(a)] to nanonails [Fig. 2(b)] is accompanied by an increase of the surface roughness r , which is defined as the ratio of the actual over the apparent surface area. According to the Wenzel model,²² the apparent CA θ_A for a rough surface is given by

$$\cos \theta_A = r \cos \theta, \quad (2)$$

which naturally explains the increase of CA from Figs. 2(a) and 2(b).

On the other hand, for the nanonails shown in Figs. 2(c) and 2(d), as the caps of nanonails grow larger, air is trapped in the grooves formed under the caps.²³ In the Cassie–Baxter model, which describes this hydrophobicity-prone situation,²⁴ θ_A is described as

$$\cos \theta_A = (1 - f_v)(\cos \theta + 1) - 1, \quad (3)$$

where f_v is the area fraction of vapor on the surface. The caps of nanonails prevent a complete contact between the water and the nonwetted surface, promoting the Cassie–Baxter state. However, a larger cap size results into a reduced f_v , therefore, a smaller θ_A . This is consistent with the decreasing trend observed in Figs. 2(c) and 2(d). Both the surface roughness and the vapor contact area play very important roles in the wetting behaviors and the detailed competing mechanisms warrant further investigations.

Besides tuning the surface morphology, adding hydrophobic terminal groups by chemical modifications is another effective method to enhance hydrophobicity. Stearic and oleic acids are commonly used due to their nontoxicity and low cost. During the surface treatments, the carboxylic acid headgroups form chelating bonds with the Zn atoms on the surfaces.¹² In order to form uniform coatings, ZnO samples were dipped in 5 mM stearic or oleic acid ethanol solution

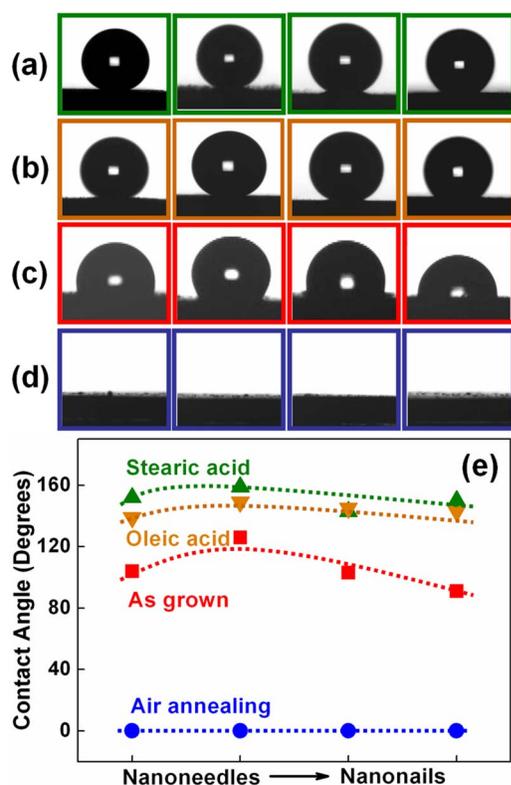


FIG. 3. (Color online) Shapes of water droplets photographed on four equally spaced positions as depicted in Fig. 2 for (a) stearic acid treated, (b) oleic acid treated, (c) as-grown, and (d) air-annealed samples. The corresponding CA were plotted in (e).

for 24 h at room temperature. They were then thoroughly washed with anhydrous alcohol and dried in air. FESEM studies of the samples showed no apparent topographical change after the fatty acid treatments. In our samples, surface modified by stearic acid achieved superhydrophobicity with a highest CA of 159° [Figs. 3(a) and 3(e)]. Modification with oleic acid resulted into slightly lower CAs [Figs. 3(b) and 3(e)].

For many applications, it is desirable to achieve surfaces which can be tuned conveniently between hydrophobicity and hydrophilicity. Annealing, as another effective surface treatment method, has been effectively used to create superhydrophilic surfaces.¹³ After the as-synthesized Cu-doped ZnO samples were annealed in air for 2 h at 400 °C, CAs of ~0° [Fig. 3(d)] were observed. The observed dramatic conversion from hydrophobicity to superhydrophilicity can be attributed to high-density oxygen-related defects created by annealing.¹³ In order to investigate the reversibility, the wetting behavior was measured again in the middle of the sample after a treatment with stearic acid as described previously. CA recovered to ~150°, indicating that superhydrophobicity is dictated by the surface chemistry and the geometrical structure. After the sample was dipped in acetone for 24 h, the surface wettability returned again to superhydrophilicity, indicating a complete coating removal. As shown in Fig. 4, this process was repeated several times and a good reversibility between superhydrophobicity and superhydrophilicity was observed.

In conclusion, vertically aligned Cu-doped ZnO hierarchical structures were shown to present complex architectures combining microscale and nanoscale features. A CA variation was observed and contributed to the effects of sur-

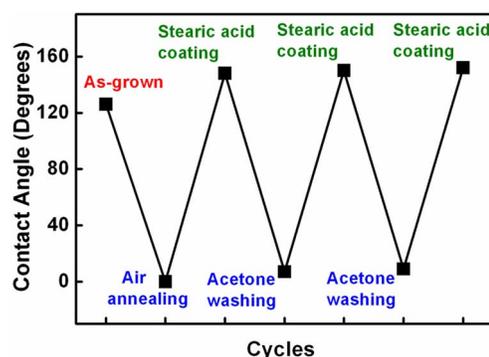


FIG. 4. (Color online) Reversible transitions between superhydrophobicity induced by air annealing and superhydrophobicity induced by stearic acid coating.

face roughness and air/water interface. Furthermore, hydrophobicity can be further enhanced by surface modifications with fatty acids. Finally, cycling between the annealing-induced superhydrophilicity and the chemically induced hydrophobicity demonstrated the highly tunable wettability in these nanostructures. Therefore, it is promising to optimize the surface wettability by designing complex hierarchical structures and making chemical modifications. Moreover, future studies on the CA hysteresis and dynamic behaviors will help to elucidate the wetting behaviors of functional materials and to pave the way for potential applications.

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