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Thermal effect on superhydrophobic performance of stearic acid modified ZnO nanotowers

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Abstract

The thermal desorption of stearic acid on superhydrophobic zinc oxide nanotowers has been investigated. The stearic acid passivated zinc oxide nanotowers provide a very high contact angle of ~173 ± 1.1° with a very low hysteresis of ~1.4 ± 0.5° due to the presence of a binary structure composed of several nanosteps on each nanotower of height ~700 nm that eventually reduces the area of contact between the drop and the nanotowers and trapping more air as revealed by the field emission scanning electron microscopy images. The superhydrophobic performance of these nanotowers, however, declines following annealing at elevated temperatures. Fourier transform infrared spectra show a reduction in the intensity of stearic acid $–CH_n$ peaks at elevated temperatures revealing the cause of the decrease in contact angle and confirming the occurrence of thermal desorption at 184 °C. The corresponding activation energy for desorption determined from our data is 0.34 ± 0.05 eV. It is found that the stearic acid has completely disappeared at 350 °C, making the sample hydrophilic.

Keywords: Superhydrophobicity; ZnO nanotowers; Thermal desorption; FTIR; Contact angle; SEM

1. Introduction

Nanostructured hybrid organic–inorganic nanocomposites present paramount advantages to facilitate the integration and miniaturization of the devices in nanotechnology [1]. Metals and metal oxide nanoparticles hybridized with organic compounds have potential applications in many technological fields such as microfluidics, tribology, biosensors, optics, catalysis, etc., and have been of considerable interest recently [2,3]. Such organic–inorganic hybrid films possess properties such as superhydrophobicity, facilitating protection from surface contamination by self cleaning, corrosion inhibition, etc. [3–7]. Several attempts have been made to produce such hybrids; however, very little effort has been made to study the chemical and thermal stability of the organic coatings [8–11]. Studies on the thermal decomposition of surfactant coatings, such as oleic acid, stearic acid and polyethylene glycol, have been carried out on nanostructured metal surfaces [12–15] Several methods have been used to study the thermal desorption of organic layers such as thermogravimetry (TGA), differential thermal analysis (DTA), temperature programmed desorption mass spectrometry (TPD-MS), etc [16]. Wang et al. [13], used TPD to study the thermal desorption of stearic acid on Pd_xNi_{1-x} composites. Pimbley and MacQueen [15] used ellipsometry to study desorption of stearic acid on platinum and nickel surfaces and Consalvo et al. [17] used atomic force microscopy (AFM) to investigate the thermal stability of stearic acid on plasma-oxidized silicon substrates. Hybrid structures of oxides and organic coatings have important applications in many fields, for example, electrical insulation, photonics, piezoelectric devices, photovoltaic devices, photocatalysis, microelectronic circuits, etc. [1,3], thus, thermal stability of these organic molecules on metal oxides is an important question. Several superhydrophobicity studies have been carried out recently on metal oxide surfaces passivated with organic molecules [18–20], however, the superhydrophobicity behavior of these organic–inorganic hybrids has not yet been investigated following exposure to elevated temperatures.

In this paper, we present highly superhydrophobic stearic acid passivated zinc oxide nanotowers and we investigate the

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thermal stability of stearic acid on these zinc oxide nanotowers by Fourier transform infrared spectroscopy (FTIR). We report the occurrence of thermal desorption of the stearic acid at elevated temperatures and correlate its effect on superhydrophobicity.

2. Experimental Section

Ultrasonically cleaned and hydrofluoric acid etched silicon substrates were immersed in a chemical bath consisting of 100 ml of aqueous 0.1 M $Zn(NO_3)_2$ and 4 ml of 28% aqueous NH_4OH solution for the growth of ZnO nanotowers via the chemical bath deposition technique (CBD). The as-prepared ZnO samples, coated at an oven temperature of 70 °C, were oven dried for more than 10 h at 70 °C, cooled to room temperature, and then passivated with 2×10^{-3} M stearic acid (SA) in acetone for 30 min by immersion. Flat ZnO samples were prepared by spin coating of 0.02 M methanolic zinc acetate solution at 3000 rpm for 30 s following annealing in air at 450 °C for 30 min. These flat ZnO samples were passivated using SA in a similar process. The microstructure of these films was investigated by a LEO field emission scanning electron microscopy (FESEM) and atomic force microscope (AFM) (Digital Nanoscope IIIa by Digital Instruments). The passivated CBD grown as well as flat ZnO samples were annealed in air for 30 min at different temperatures ranging from 70 to 350 °C for thermal desorption studies. The thermal desorption of SA on CBD ZnO was monitored using Fourier transform infrared spectroscopy (FTIR) (PerkinElmer Spectrum One) after each annealing treatment. Ultrasonically clean silicon substrate was used for background subtraction during FTIR measurements and the number of scans used for each samples annealed at different temperatures were kept constant at 20. These samples were tested for superhydrophobicity using a contact angle goniometer (Krüss GmbH, Germany). A very standard and commonly used experimental procedure as reported in the literature [21] was followed to measure the contact angle hysteresis, which is the difference between the advancing and receding contact angle. In this method, water drops of volume ~5 μL is suspended with the needle and brought in contact with the superhydrophobic surfaces using a computer controlled device as provided by Krüss GmbH. The advancing and receding contact angles are measured by holding the water drop with a stationary needle in contact with the surface and moving the contact angle goniometer stage in one direction. The contact angle data were acquired by fitting the symmetric water drops using the Laplace–Young equation and the advancing and receding contact angles were measured by fitting the asymmetric water drops using the tangent-2 method [22]. X-ray diffraction was carried out using Cu Kα radiation in a Bruker D8 Advance diffractometer in order to study the crystal structure of the CBD ZnO samples after annealing at elevated temperatures.

3. Results and discussion

The growth process of ZnO nanotowers involves a chemical reaction during which the zinc nitrate decomposes to give ZnO

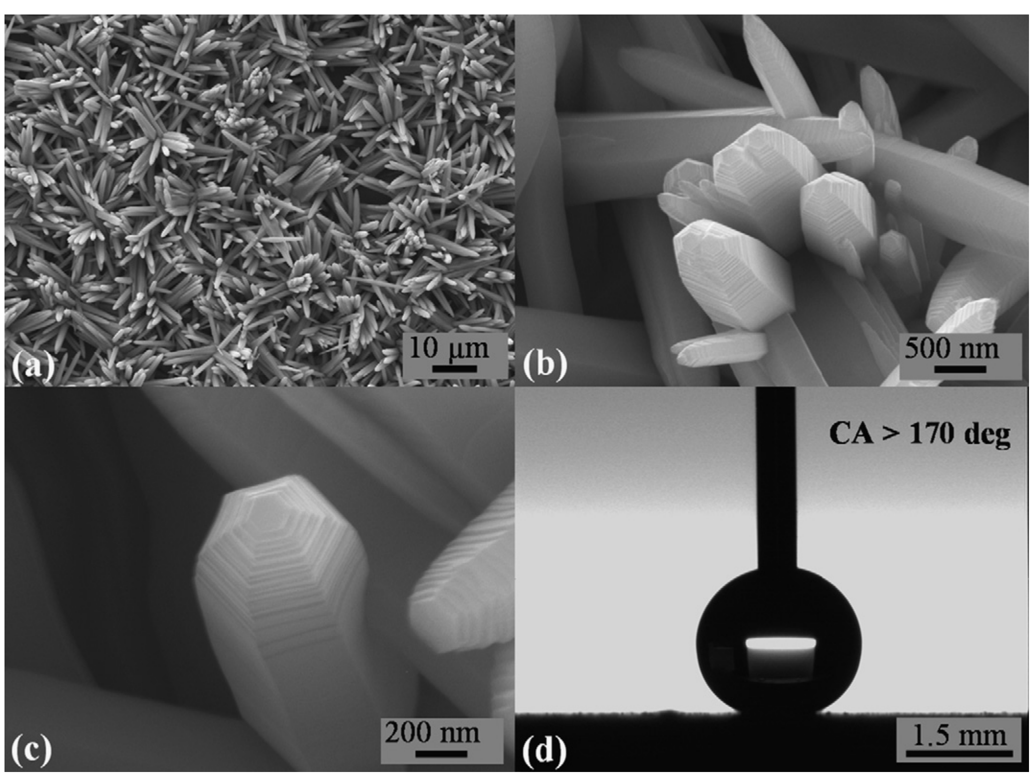

Fig. 1. FESEM images of ZnO nanotowers at (a) low magnification (b) ZnO nanotowers at high magnification showing the hexagonal morphology; (c) close up view of a single nanotower showing the nanosteps; (d) image of a water drop on the surface of these nanotowers after SA passivation.