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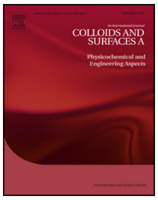


Wetting behavior of triethoxyoctylsilane modified ZnO nanowire films

C.L. Xu, L. Fang*, F. Wu, Q.L. Huang, B. Yin

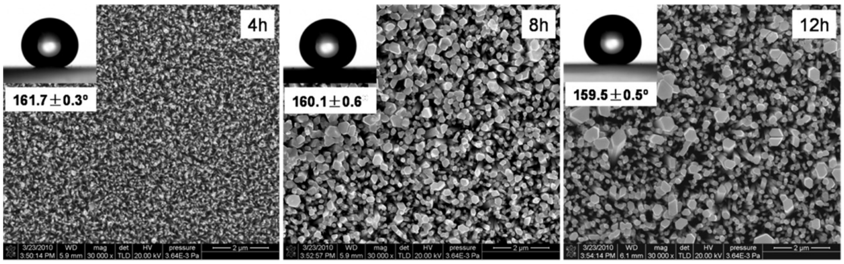
State Key Laboratory of Power Transmission Equipment & System Security and New Technology, College of Physics, Chongqing University, Chongqing 400044, PR China

HIGHLIGHTS

- Well-aligned ZnO nanorod films were prepared onto a spin-coated ZnO seed layer.
- The growth time has effect on the structure and morphology.
- The effect of growth time on the hydrophobicity of ZnO nanorod films was analyzed.
- The contact angle and sliding angle of the superhydrophobic surface are 161.7° and 6°.

GRAPHICAL ABSTRACT

Superhydrophobic ZnO surfaces with tunable high water adhesion have been fabricated by combining both a simple solution chemistry approach and ethanol solution of triethoxyoctylsilane.



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ABSTRACT

ZnO nanowire films have been prepared by chemical process at 90 °C for different growth time varied from 4 h to 12 h. The effect of growth time on the structure, morphology, and the hydrophobicity of ZnO nanowire films were investigated. The results indicate that all of the films exhibit the hexagonal wurtzite phase with growth direction perpendicular to the substrate surface. The scanning election microscopy images of ZnO nanowire films show that prolonging the growth time results in longer nanowires with uneven diameter. The influence of the diameter of nanowires on the wettability of the film was analyzed. Typically, the film prepared for 4 h exhibits a high water contact angle of about 161.7 ± 0.3° with the advancing contact angle of 157.2 ± 0.5° and receding contact angle of 163.2 ± 0.5° and a small sliding angle of 6° after hydrophobic treatment. Based on the Cassie theory, the analysis results reveal that only about 6% of the water surface contacts with the ZnO films and the remaining 94% contacts with the air cushion, which is reasonable for the hydrophobicity of a ZnO nanowire films.

1. Introduction

The wetting behavior of a solid surface is one of the most important aspects of surface physical chemistry, and depends on the chemical composition as well as the geometric structure of the surface [1–4]. Wettability directly affects various life activities in nature and controlling the wetting property of the surface is of vital importance for a wide range of biological, chemical and electronic applications [5,6]. For a solid surface, when a contact angle of water on it is larger than 150°, it is called superhydrophobic surface which can repels water extremely [7]. The optimum surface morphologies to achieve high hydrophobicity are micro-nano-binary structures with low surface free energy, which is concluded from nature [8]. In recent years, such surfaces have attracted much attention owing to their important applications, such as microfluidic devices [9–11] and self-cleaning materials [12,13].

As a II–VI compound semiconductor, wurtzite zinc oxide (ZnO) has a direct wide band gap of 3.3 eV and a strong exciton binding energy of 60 meV [14], and the thermal energy at room

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* Corresponding author. Tel.: +86 23 65678369.
E-mail addresses: lingling19880210@126.com (C.L. Xu), lfang@cqu.edu.cn (L. Fang).

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temperature (26 meV), which can ensure an efficient excitonic emission at high temperature under low excitation energy. It has attracted much attention in recent years due to its many potential applications, such as sensors, capacitors, semiconductor lasers, fluorescent materials and conductive materials [15–19]. Except for these applications, low dimensional ZnO materials such as ZnO nanowire arrays have been used to generate superhydrophobic surface due to the minimum of water–solid contact fraction of this sort of structures, and the superhydrophobicity was obtained in many cases after grafting organic monolayer or depositing hydrophobic material layers [2,20–22]. Various deposition techniques have been employed to prepare ZnO nanowire films such as chemical vapor deposition [23], hydrothermal technique [24], electrochemical deposition [25], pulsed laser deposition [26], etc. In resent years, some groups have studied the wetting behavior of ZnO nanoarray films. A surface-modification-induced hydrophilicity to superhydrophobicity transition on well-aligned ZnO nanorod array films by different methods was reported [27–31]. Chang and Hung found that by controlling the surface nanostructure, the wettability of films with similar pore-array microstructure can be tuned from hydrophilic to nearly superhydrophobic without variation of the chemical composition [32]. Feng et al. investigated the reversible super-hydrophobicity to super-hydrophilicity transition of aligned ZnO nanorod films [33]. Herein, well-aligned ZnO nanowire films were prepared by two-step method, which means ZnO nanowires were prepared by liquid phase method on a sol–gel spin-coated ZnO seed layer. Moreover, the super-hydrophobic surface was achieved by modifying the surface of as-grown ZnO nanowire films with triethoxyoctylsilane. The procedure was easy to carry out, and no special equipment was required. The effect of growth time on the structure, morphology, and the hydrophobicity of ZnO nanowire films were analyzed. The findings could substantially enlarge the application of ZnO based nanostructures.

2. Experimental

2.1. Materials

Fluorine-doped SnO_2 (FTO) purchased as the substrate. Zinc acetate, and hexamethylenetetramine (HMTA) purchased from Sinopharm Chemical Reagent Co., Ltd., China, involved for ZnO nanowire growth; triethoxyoctylsilane (KH-832, Shanghai Ruicong Analytical Instrument Co., Ltd.) was used for modifying the surface of as-grown ZnO nanowire films. All of the solvents and chemicals used in this study were of reagent grade.

2.2. Sample preparation

In this study, the growth of ZnO nanowires was conducted by two steps: (1) the formation of crystal nucleus as seeds by spin coating process with ZnO sol [34], and (2) the formation and growth of the nanowires. The FTO substrates were ultrasonically cleaned in acetone and deionized water, respectively, for 30 min. Then the substrates were spin coated with 0.015 M zinc acetate in ethanol, then dried at 100 °C for 20 min, this process was repeated five times. After that, the substrates were treated at 380 °C for 1 h to form ZnO nanocrystals which were used as seeds for subsequent growth of ZnO nanowires by thermal decomposition of zinc acetate. Each seeded substrate was then placed vertically in a 40 mL growth solution consisting of 0.025 M zinc acetate and 0.025 M HMTA in deionized water. The container was covered and placed in a water bath preheated to 90 °C to start the growth of ZnO nanowire. This growth progress was lasted 4, 8 and 12 h by changing the growth solution every 4 h. The ZnO nanowires were taken out to rinse with deionized water for several times and annealed in air at 450 °C for 30 min to remove any residual organics.

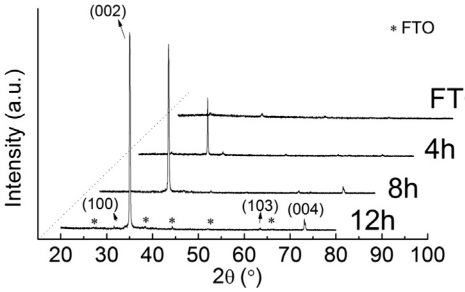

Fig. 1. XRD patterns of FTO substrate and the ZnO nanowire films prepared at 90 °C for different growth time.

The surface of as-grown ZnO nanowire films were chemically modified by dipping in a 2.0 wt.% ethanol solution of triethoxyoctylsilane for 24 h at room temperature, subsequently heated at 160 °C for 1 h.

2.3. Measurements

The crystal structure of the samples was examined by X-ray diffraction (XRD) with a MRD-Single Scan diffract-meter using the Cu Kα line ($\lambda = 1.5406$ Å). The power of XRD was 1200 W and the scan was performed from 20° to 80° at a speed of 4°/min, with a step size of 0.01°. The surface morphologies of the obtained samples were observed on a field emission scanning electron microscope (FESEM, Nova 400). The operating voltage of FESEM is 10.00 kV. The thickness of the nanowire films were measured by a step profiler (Dektak 150). Contact angles were measured with a contact angle meter (Drop Meter TM A-100P) at ambient temperature and the sliding angle was measured by the conventional tilting plate method. The volume of water drops was 8 μL. The water contact angles (WCA) were measured at five different spots for each sample, and the average value was adopted as the final result of the contact angle. Besides, the error analysis of the data of WCA was implemented by arithmetic mean of the root mean square error. A X-ray photoelectron spectroscope (XPS, PHI-multifunctional XPS, Kratos Corp., England operating with MgKα irradiation ($h\nu = 1253.6$ eV) was used to analyze the chemical states of some typical elements distributed on the hydrophobic surface. The emission source is Mg and the voltage and emission current of the excitation electron beam was set to 14 kV and 120 mA, respectively. The energy scale was internally calibrated by referencing to the binding energy (E_b) of the C_{1s} peak of a carbon contaminant at 284.6 eV.

3. Results and discussion

3.1. Structural and morphological properties of ZnO nanowire films

Fig. 1 shows XRD patterns of FTO substrate and ZnO nanowire films prepared at 90 °C for different growth time. All the films exhibit a strong diffraction peak of (0 0 2) and several weak peaks such as (1 0 0), (1 0 3) and (0 0 4), which are consistent with the hexagonal wurtzite phase of ZnO. Besides, the intensity of (0 0 2) peak is much stronger than other diffraction peaks, indicating the nanowires have preferential orientation along the c-axis perpendicular to the substrate. It also reveals that the intensity of the diffraction peaks of (0 0 2) and (0 0 4) increases with the growth time, which is attributed to the film thickness enhancing from 1 μm (4 h) to 7.3 μm (12 h).

The FESEM images of the FTO substrate and the ZnO seed layer coated on FTO substrate are given in Fig. 2. It shows that the