



ZnO nanowires grown directly on zinc foils by thermal oxidation in air: Wetting and water adhesion properties



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ABSTRACT

Large scale ZnO nanowire arrays were grown directly on zinc foils using the thermal oxidation in air method. The X-ray diffraction and reflectance investigations confirm that the as-grown nanowires properties are typical for ZnO having a hexagonal wurtzite crystalline structure and band-gap values between 3.2 and 3.3 eV. The scanning electron microscopy images prove that the density and the dimensions (diameter and length) of the ZnO nanowires can be tuned by controlling the oxidation temperature. Wettability studies reveal in the case of Zn foils a hydrophilic behavior with high water droplet adhesion which is transformed into a superhydrophobic one with low water droplet adhesion after the foils' surfaces are covered with ZnO nanowires. Obtaining functional surfaces with such interesting wetting properties using a simple, inexpensive and highly reproducible thermal oxidation in air technique is very attractive for anticorrosion coatings and self-cleaning applications.

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1. Introduction

ZnO nanowires are one of the most studied metal oxide nanostructures due to their unique surface to volume ratio-dependent properties and to their wide potential applications in electronics, optoelectronics, sensors, energy harvesting devices, superhydrophobic surfaces, etc. [1–5]. Besides the remarkable intrinsic characteristics, these ZnO one-dimensional nanostructures are biologically compatible and environmental-friendly. During the last years, the surface related properties of ZnO nanowires, especially the superhydrophobic behavior, have attracted considerable research attention because of their technological applications in the areas of anticorrosion coatings and self-cleaning surfaces [4–10]. Among the various physical and chemical preparation routes employed for growing the ZnO nanowires like chemical vapor deposition, pulsed laser deposition, electrochemical or hydrothermal methods [2–5], thermal oxidation is a relatively facile, low-cost and non-hazardous technique [11,12]. Moreover, direct oxidation in air, oxygen or other gases of a metallic Zn substrate in the form of film [9,10], powder [13], wire [14] or foil [15] is a non-catalytic approach for large-scale growth of high purity ZnO nanowires. An important role in the thermal oxidation process is played by the temperature parameter, which varies typically from 200 °C to 1000 °C. Taking into account the melting temperature (420 °C) and the boiling temperature

(907 °C) of zinc, the oxidation mechanism of Zn can vary with the annealing temperatures and in this way the morphology of the grown ZnO nanostructures can be modified from nanowires to tetrapods, when the applied temperatures are below the zinc melting point or between the melting and boiling points of zinc or above the Zn boiling point, respectively [16]. Although, some papers were focused on the thermal oxidation growth of ZnO nanowires and their structural and optical characterization [9–16], very few tackle the surfaces' wettability of the grown ZnO nanowires on Zn film [9,10] and none, to our knowledge, on Zn foil.

In the present work, ZnO nanowires were grown using thermal oxidation in air directly on Zn foils. The structural, optical and morphological properties of the prepared ZnO nanowires arrays were studied. The density and dimensions of the semiconducting nanowires were easily manipulated by changing the annealing temperature. Furthermore, the wetting and water adhesion characteristics of the Zn foils covered with ZnO nanowires were investigated in order to explore their utility, a superhydrophobic behavior with low water adhesion being evidenced. Therefore, this simple, cost efficient and environmentally friendly preparation technique giving scalable and reproducible superhydrophobic ZnO nanowires might be successfully used for a very effective corrosion-resistant coating for the underlying zinc and for self-cleaning applications.

2. Experimental

A Zn foil (Alfa Aesar, 99.98% purity and 0.25 mm in thickness)

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was cut in pieces having approximately 2 cm². The metal substrates were cleaned in acetone and isopropyl alcohol for 5 min in an ultrasonic bath, followed by repeated rinsing in deionized water and dried under nitrogen gas flow. Next, in a convection oven, the Zn foil samples were annealed in air for 12 h at 400 °C, 500 °C and 600 °C. A visual detail suggests the formation of a metal oxide layer after the annealing process: the metallic luster of Zn foil is lost acquiring the typical whitish color of ZnO. Also, at oxidation temperatures higher than the zinc melting point, the flat aspect of the foil is changed into a wrinkled one.

The structural, optical and morphological properties of the samples were evaluated using a Bruker AXS D8 Advance instrument with Cu K α radiation ($\lambda=0.154$ nm), a Perkin-Elmer Lambda 45 UV–vis spectrophotometer equipped with an integrating sphere and a Zeiss Evo 50 XVP scanning electron microscope. The wetting properties of the thermally oxidized zinc foils were determined by measuring the static contact angle (CA) with a Drop Shape Analysis System, model DSA100 from Kruss GmbH. The detailed processes of the water droplet adhesion behaviors at the surface of the samples were recorded by a video camera.

3. Results and discussion

The X-ray diffraction (XRD) and reflectance measurements were made in order to evaluate the crystalline phases and the band gap values of the as-grown metal oxide obtained after annealing. The XRD patterns of all thermally oxidized Zn foils (Fig. 1a), are similar exhibiting mixed diffraction peaks indexed to Zn and ZnO. Thus, in addition to the peaks assigned to the underlying Zn substrate (JCPDS file no. 04-0831) the other present peaks in the diffraction patterns confirm the formation of ZnO being indexed to its hexagonal wurtzite phase (JCPDS file no. 36-1451). Based on the reflectance data, the band gap of ZnO was estimated around 3.2–3.3 eV by representing the Kubelka–Munk function (Fig. 1b), where $F(R)=(1-R)^{1/2}/2R$ and R was the observed diffuse reflectance. For all samples, the ZnO band gap value is in agreement with previously reported data for ZnO nanowire-like structures synthesized by chemical vapor deposition or hydrothermal methods [17].

The surface morphology of the metallic substrate and the thermally oxidized Zn foils was analyzed by scanning electron microscopy (SEM), the images being presented in Fig. 2, at low and high magnifications. The Zn foil has a relatively flat surface (Fig. 2a) which wrinkles with increasing the oxidation temperature, together with the formation of ZnO nanowires (Fig. 2b–d). At

400 °C, on the metallic surface, the grown nanowires are scarcely distributed, having diameters of about 40 nm and lengths up to 3 μ m (Figs. 2b and b'). At higher oxidation temperature, the whole Zn foil surface is completely and uniformly covered with ZnO nanowires (Figs. 2c and d) with larger diameters and longer lengths. At 500 °C, the nanowires have diameters of about 60 nm and lengths up to 40 μ m (Fig. 2c'), while at 600 °C the diameters reach at about 80 nm and the lengths up to 60 μ m (Fig. 2d'). Some of the nanowires' features must be emphasized: the relatively uniform size distribution for each oxidation temperature, the smooth surface and the high aspect ratio.

The functionality of the thermally oxidized metallic substrates was evidenced by investigating the wetting properties while measuring the water contact angle (CA) on these surfaces (Fig. 2 insets) and observing the water droplets adhesion behavior (Fig. 3). As seen in Fig. 2, a transition from a hydrophilic surface, in the case of the metallic foil before annealing, to a superhydrophobic one, for the foil surface covered with ZnO nanowires occurs.

Furthermore, with respect to the water droplets' adhesion it was found that the water droplet was highly adherent to the surface of the Zn foil (Fig. 3a₁–a₅) and also to the surface of the foil treated at 400 °C which contains only few ZnO nanowires (Fig. 3b₁–b₅), resting stick, firmly pinned on the samples' surfaces even when these were turned upside down. Instead, in the case of the foils having the surfaces entirely covered with ZnO nanowires, the water droplets slid when these were tilted to a vertical position (Fig. 3c₁–c₅) or rolled off very easily at slight tilt (Fig. 3d₁–d₅).

In order to find an explanation for these results, we used the Cassie–Baxter relation in the form: $\cos\theta^*=\phi_S(\cos\theta_E+1)-1$ [5], where θ^* was the CA formed on thermally oxidized samples, θ_E was the CA formed on pure Zn foil (CA=86.3°) and ϕ_S parameter was the fraction of the surface in contact with the water droplet. The following values of the ϕ_S were obtained: 0.8 (for CA=98.6°), 0.08 (for CA=156.0°) and 0.03 (for CA=165.1°). So, based on the small ϕ_S values, the wetting and adhesion properties of the Zn foil completely covered with ZnO nanowires can be understood if the water droplet is considered in contact with the ZnO nanowire surface only in few small sites, the space between the randomly grown nanowires being filled with a large volume of air. Such surfaces with superhydrophobic behavior and low water droplet adhesion are effective for anticorrosion covering and self-cleaning uses.

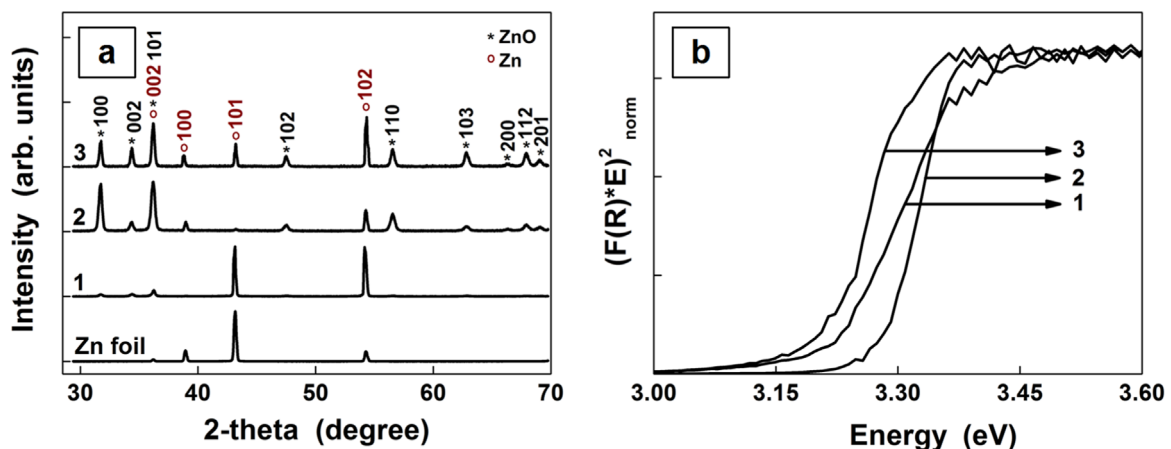


Fig. 1. XRD patterns (a) and representations of the Kubelka–Munk function employed to estimate the band gap value (b) for the ZnO nanowires arrays grown on Zn foils at: 400 °C (curve 1), 500 °C (curve 2) and 600 °C (curve 3).

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