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A General Low-Temperature Route for Large-Scale Fabrication of Highly Oriented ZnO Nanorod/Nanotube Arrays

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As a wide band gap semiconductor oxide with a large excitation binding energy (60 meV), zinc oxide becomes one of the most important functional materials with unique properties of near-UV emission, optical transparency, electric conductivity, and piezo electricity. Since the first report of ultraviolet lasing from ZnO nanorods,¹ substantial effort has been devoted to the development of novel synthetic methodologies for one-dimensional (1D) ZnO nanostructures due to their promising applications in electronic and optoelectronic devices.² Currently, large-scale low-cost controllable growth of well-aligned ZnO nanorods on properly fitting substrates is crucially expected for these novel applications.³ As the widely used high-temperature vapor-phase processes are expensive and energy-consuming,⁴ various solution-phase approaches to ZnO nanorods have recently attracted extensive interest because of their low growth temperatures (90–95 °C) and good potential for scale-up.⁵ Among these reported approaches, the most successful one is based on the seeded growth of well-oriented ZnO nanorod arrays on ZnO-nanoparticle-coated substrates.⁶ However, the liquid-phase coating of the substrates with ZnO nanoparticles prepared in solution remains complex and difficult/irreproducible. Here, a conventional radio frequency magnetron-sputtering technique was utilized to simply prepare ZnO-film-coated substrates for subsequent growth of highly oriented ZnO nanorods. The highly oriented ZnO nanorods can be easily fabricated on ZnO-film-coated (arbitrary) substrates over a large area via a simple low-temperature solution route. This novel synthetic approach also allows further reducing the growth temperature to 65 °C, leading to the development of an effective and low-cost fabrication process for high-quality ZnO nanorod arrays. Moreover, we report the low-temperature synthesis of hexagonal ZnO nanotube arrays, which can be formed on zinc foils in the same reaction system.

Typically, one ZnO-film-coated substrate and two 7 mm × 7 mm zinc foils were immersed in 3 mL of 5% formamide aqueous solution (v/v) in a 10-mL sample vial followed by 24-h heating at a constant temperature of 65 °C. They were then rinsed with ethanol and dried in air for further characterization. Figure 1A clearly shows a large-area array of ZnO nanorods grown on ZnO-film-coated glass substrates. The whole substrate surface was successfully covered with uniform and dense arrays of hexagonal ZnO nanorods of ~100 nm in diameter. The flat surface indicates identical lengths of ZnO nanorods of ~1 μm (Supporting Information). The XRD pattern of the nanoarrays shows only a sharp (002) diffraction peak at 34.26° (full width at half-maximum: ~0.6–0.7°),^{6c} indicating the highly preferential growth of ZnO nanorods along the *c*-axis orientation (perpendicular to the substrate surface). The obtained strong near-UV emission peak of ZnO nanorod array centered at 400 nm is attributed to near band-edge transition.⁷ Furthermore, a ZnO nanotube array (Figure 1B) was observed on the surface of zinc foil. The diameters of the ZnO nanotubes range from 200 to 300 nm. The inset of Figure 1B reveals a high-magnification SEM

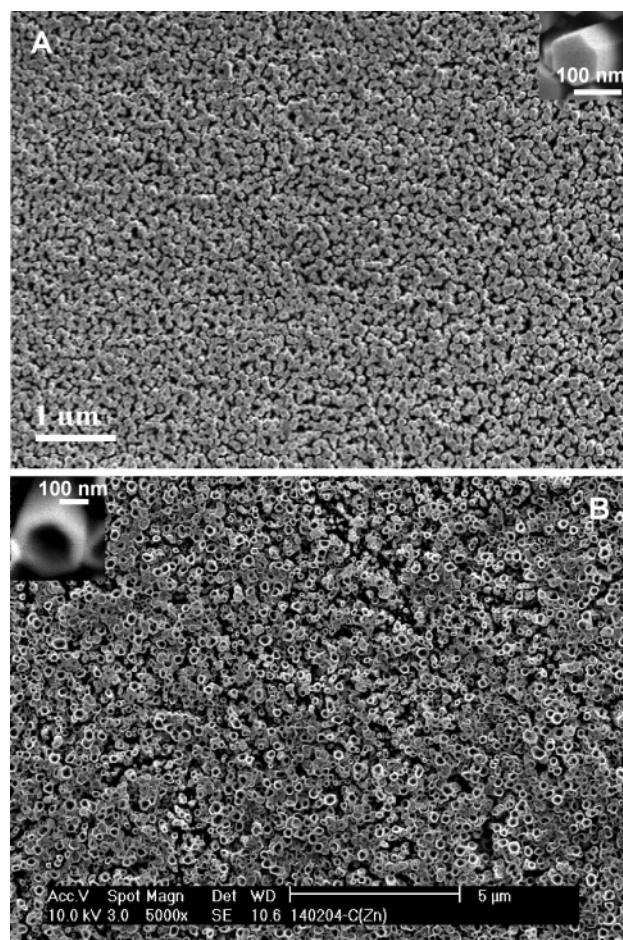


Figure 1. SEM images of large-scale dense arrays of well-aligned (A) ZnO nanorods and (B) ZnO nanotubes grown on ZnO-film-coated glass substrate and zinc foil, respectively, in 5% formamide aqueous solution at 65 °C. Top views of one nanorod and one nanotube are shown in the inset high-magnification SEM images.

image of one ZnO nanotube, showing a perfect hexagonal shape with a diameter of ~250 nm and uniform wall thickness of ~30 nm.

Figure 2A shows that the surface of ZnO-film-coated glass substrate (~150 nm in thickness), prepared by a radio frequency magnetron-sputtering technique, was densely covered by ZnO nanoparticles with a mean diameter of ~60 nm derived from the inset AFM image. The sputtered ZnO film was also textured along the *c*-axis, indicated from the only (002) diffraction peak.⁸ After the subsequent growth of ZnO nanorods, the obtained XRD pattern is the same but with enhanced intensity, indicating the epitaxial growth of ZnO nanorods on the oriented ZnO film. To understand the seeded growth of ZnO nanorods, the time-dependent kinetic

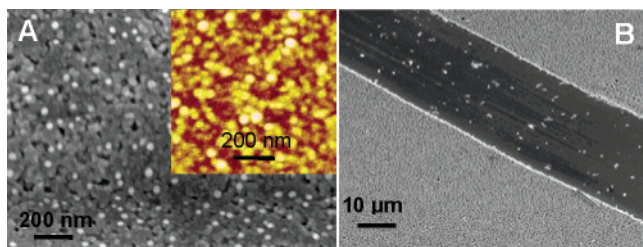


Figure 2. (A) SEM and inset AFM images of the ZnO-film-coated glass substrate. (B) SEM image of patterned growth of ZnO nanorods on the ZnO-film-coated substrate.

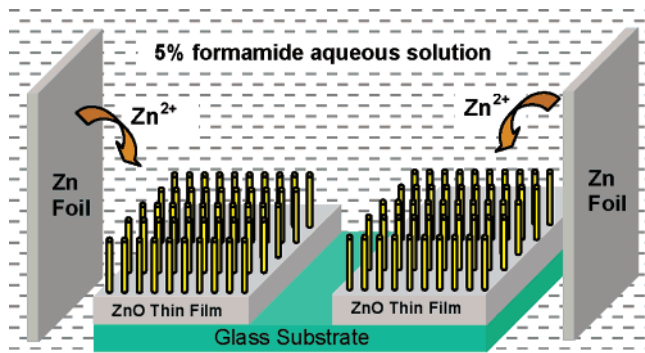


Figure 3. Schematic illustration of the growth of ZnO nanorods on a patterned substrate.

process (Supporting Information) and the substrate effect were further studied. Figure 2B shows the patterned growth of ZnO nanorods on the patterned ZnO strips with a spacing of $\sim 30 \mu\text{m}$ on glass substrate. No ZnO nanorods were found on the spacing area where only glass was exposed, and ZnO nanorod arrays covered only the surface of ZnO film because the ZnO may lower the lattice mismatch between the deposition and the substrate.

Figure 3 shows a schematic illustration of the growth of 1D ZnO nanostructures. Zinc precursors were continuously supplied from metal zinc in formamide solution.⁹ As a result, there is a gradient in the concentrations of zinc precursors from Zn foil to ZnO-film-coated substrate in solution. At the lower concentration region around the ZnO-film-coated substrate, the diffusion rate of zinc precursors is relatively fast with respect to that of crystal growth at the liquid–solid interface.¹⁰ The concentration of zinc precursors is uniform throughout the surface of seed particles on ZnO-film-coated substrate, and growth takes place on entire seed particles, giving rise to solid nanorods.¹⁰ At the higher zinc concentration region near the zinc foil, the growth rate has increased with respect to the rate of diffusion, and the zinc concentrations are largely decreased close to the top area of 1D ZnO nanostructures, leading to the preferential growth of nanowalls and limiting the growth of nanorods.¹⁰ On the other hand, the mean diameter of ZnO nanorods grown on ZnO-film-coated substrate ($\sim 100 \text{ nm}$) is much smaller than that of nanotubes grown on zinc foils ($\sim 250 \text{ nm}$) (Figure 1) because of the much higher seed density on the ZnO-film-coated substrate than that of the nucleation sites on the native oxide layer of zinc foil. The resulting thinner nanorods on ZnO-film-coated substrates are more stable due to their small top areas of polar metastable (001) surfaces and large lateral areas of the most stable low-index nonpolar surfaces (parallel to the c -axis).¹¹ However,

on zinc surfaces, it may not be energetically favorable to form thicker, solid ZnO nanorods due to their large top areas of metastable (001) surfaces. Instead, the formation of thicker, hollow ZnO nanotubes can reduce the top metastable areas and enlarge the lateral areas of the most stable low-index nonpolar surfaces with respect to those of the corresponding solid nanorods.

In summary, large-scale arrays of highly oriented ZnO nanorods can be formed on ZnO-film-coated substrates of any kind (glass, silicon, poly(ethylene terephthalate), etc.) using a simple low-temperature liquid-phase method. This novel soft-solution approach was also used to produce nanorod arrays on other substrates coated with indium tin oxide (ITO), Al-doped ZnO, etc. This selectively patterned growth of ZnO nanorod arrays on patterned substrates is crucial to the design of electronic and optoelectronic devices and provides a promising technique for a wide variety of potential applications. Additionally, hexagonal ZnO nanotube arrays were grown on zinc foils, and a growth mechanism is proposed.

Supporting Information Available: XRD, SEM, and TEM analysis of ZnO nanorod arrays. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) The oxidation of metal zinc by naturally dissolved oxygen is very slow in water due to the surface-passivated oxide layer. However, in the presence of formamide, the spontaneous atmospheric oxidation process can be accelerated at room temperature to release zinc ions into reaction solution through the formation of zinc–formamide complexes. More zinc–formamide complexes can be supplied continuously at an elevated temperature. At an optimized temperature of 65°C in 5% formamide aqueous solution, high-quality ZnO nanoarrays can be produced readily by this simple chemical-liquid-deposition approach during a period of 24 h of reaction. In the temporal evolution of zinc oxidation, zinc concentration increased proportionally with reaction time due to the continuous release of zinc ions into solution, and Zn complexes can be accumulated up to 0.46 mM gradually after 24 h in our preparation system. Freshly produced Zn ions can be supplied continuously for the subsequent crystal growth of nanorods on the seed particles through the thermal decomposition of the resulting zinc–formamide complexes.
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