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Elaboration and characterization of Al doped ZnO nanorod thin films annealed in hydrogen

Wen-Wu Zhong[a], Fa-Min Liu[a,*], Lu-Gang Cai[a], Peng-Ding[a], Chuan-Cang Zhou[a], Le-Gui Zeng[a], Xue-Quan Liu[b], Yi Li[b]

[a] Department of Physics, School of Physics and Nuclear Energy Engineering, Key Laboratory of Micro-nano Measurement-Manipulation and Physics (Ministry of Education), Beijing University of Aeronautics and Astronautics, Beijing 100191, China
[b] Central Iron & Steel Research Institute, Beijing 100081, China

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ABSTRACT

ZnO thin films doped with Al concentrations of 1.0, 2.0, 3.0, 4.0, 5.0 at% were prepared by a sol–gel spin-coating method on glass substrates and respectively annealed at 550 °C for 2 h in hydrogen and air. The X-ray diffraction and selected-area electron diffraction results confirm that the Al doped ZnO thin films are of wurtzite hexagonal ZnO. The scanning electron microscope results indicate that the Al doped ZnO nanorod thin films can be got by annealing in hydrogen rather than in air. The optical properties reveal that the Al doped ZnO thin films have obviously enhanced transmittance in the visible region. The electrical properties show that the resistivity of 1.0 at% Al doped ZnO thin films has been remarkably reduced from 0.73 Ω m by annealing in air to 3.2×10^{-5} Ω m by annealing in hydrogen. It is originated that the Al doped ZnO nanorod thin films annealed in hydrogen increased in electron concentration and mobility due to the elimination of adsorbed oxygen species, and multicoordinated hydrogen.

1. Introduction

One-dimensional nanomaterials have attracted a great deal of attention owing to their potential applications in nanoelectronics and optoelectronics [1–3] since first discovery of carbon nanotubes. ZnO, with wider direct band-gap energy of 3.37 eV and larger exciton binding energy of 60 meV [4–6], is a very attractive material for optoelectronic applications [7]. In the advent of nanoelectronics, one-dimensional ZnO-based heterostructure devices have recently drawn more and more attention. These ZnO nanorods have been intensely studied because of their unique properties which are derived from their low dimensionality [8]. For example, Huang et al. found that gas sensors fabricated using ZnO nanorods with faster charge diffusion rate have superior sensitivity, short response time, and well repeatability [9]. Hence, one of the most important issues to be addressed is to obtain one-dimensional ZnO thin film. In the past few years, a number of studies have been conducted to obtain the ZnO nanorods thin film [10–13]. However, there are relatively few publications that reported the Al doped ZnO nanorods thin films by annealing in hydrogen [14]. In this paper, we have reported the Al doped ZnO nanorod thin films deposited on glass substrate by sol–gel spin-coating method and annealed in hydrogen. It is found that the shape of films consists of nanorod, the resistivity is dramatically decreased by annealing in hydrogen at 550 °C for 2 h, and the films are also transparent in the visible region.

2. Experimental details

The Al doped ZnO thin films were prepared onto glass substrates by the sol–gel spin-coating method. Zinc acetate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (≥99.0%) was used as a starting material. Ethylene glycol monomethyl ether ($C_3H_8O_2$), ethanolamine (C_2H_7NO), and aluminium chloride ($AlCl_3$) (≥99.0%) were used as solvent, stabilizer, and doping source, respectively. Required quantities of $AlCl_3$ were added into zinc acetate to obtain sols with Al concentrations of 1.0, 2.0, 3.0, 4.0, 5.0 at%, respectively. The concentration of the solutions is 0.8 mol/L. The obtained mixture was stirred at 60 °C for 4 h to yield a clear and homogeneous solution, which then served as the coating source after being cooled down to room temperature. The glass substrates were first cleaned by detergent, then in methanol and acetone by using an ultrasonic cleaner, each for 30 min. Finally, the glass substrates were rinsed with deionized water and dried in oven. The coating solution was dropped onto a glass substrate, which was rotated at 3000 rpm for 30 s using KW-4A spin coater. After spin coating, the films were dried at 350 °C for 20 min in a furnace to evaporate the solvent and to remove organic residuals. This coating/drying procedure was repeated for nine

* Corresponding author. Tel.: +86 10 82338602; fax: +86 10 82338602.
E-mail addresses: fmliu@buaa.edu.cn, tianmenwenwu@163.com (F.-M. Liu).

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times before the films were inserted into a tube furnace and annealed at 550 °C for 2 h in hydrogen (no flow) and air. This coating process was applied to all samples.

The crystal graphic interpretations were performed on Rigaku D/MAX-RB X-ray diffractometer (XRD) using Cu Kα wavelength (λ = 0.154059 nm) and scanning in a 2θ range from 20° to 80°. Surface morphology and thickness of the films were studied via a FEI-SIRION scanning electron microscope (SEM). Transmission electron microscope (TEM) micrographs and selected-area electron diffraction patterns were obtained on a PHILIPS-CM200 and JEM-2010 type TEM. Optical transmittance was recorded with a double beam TU-1901 UV–vis that is spectrophotometer in a wavelength range of 350–800 nm. The conductivity measurements were performed using the four point probe method (probe: tungsten carbide, probe diameter: 0.5 mm, probe distance: 1 ± 0.01 mm, probe pressure: 5–16 N).

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows X-ray diffraction patterns of the Al doped ZnO thin films with different concentrations, annealed at 550 °C for 2 h and prepared on glass substrates by the sol–gel spin-coating method. The samples of A, B, C, D, and E annealed in hydrogen, denote the concentration of Al of 1.0, 2.0, 3.0, 4.0, and 5.0 at%, respectively. As a contrast, Fig. 1 also shows the sample of F annealed in air with the concentration of Al of 1.0 at%. The diffraction peaks in Fig. 1 can be indexed to a hexagonal wurtzite structure with lattice constants

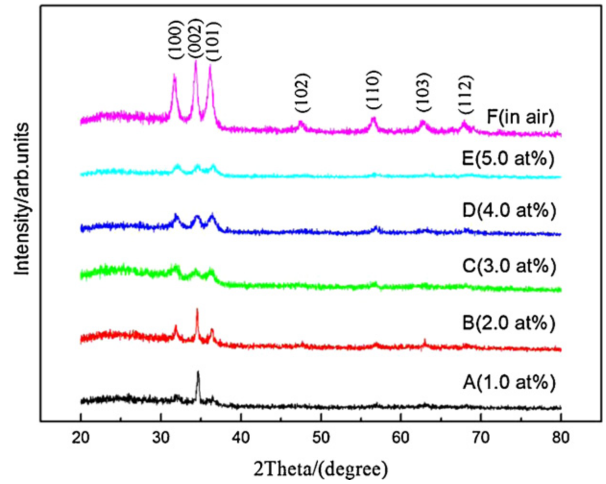

Fig. 1. X-ray diffraction patterns of the Al doped ZnO nanorods thin films.

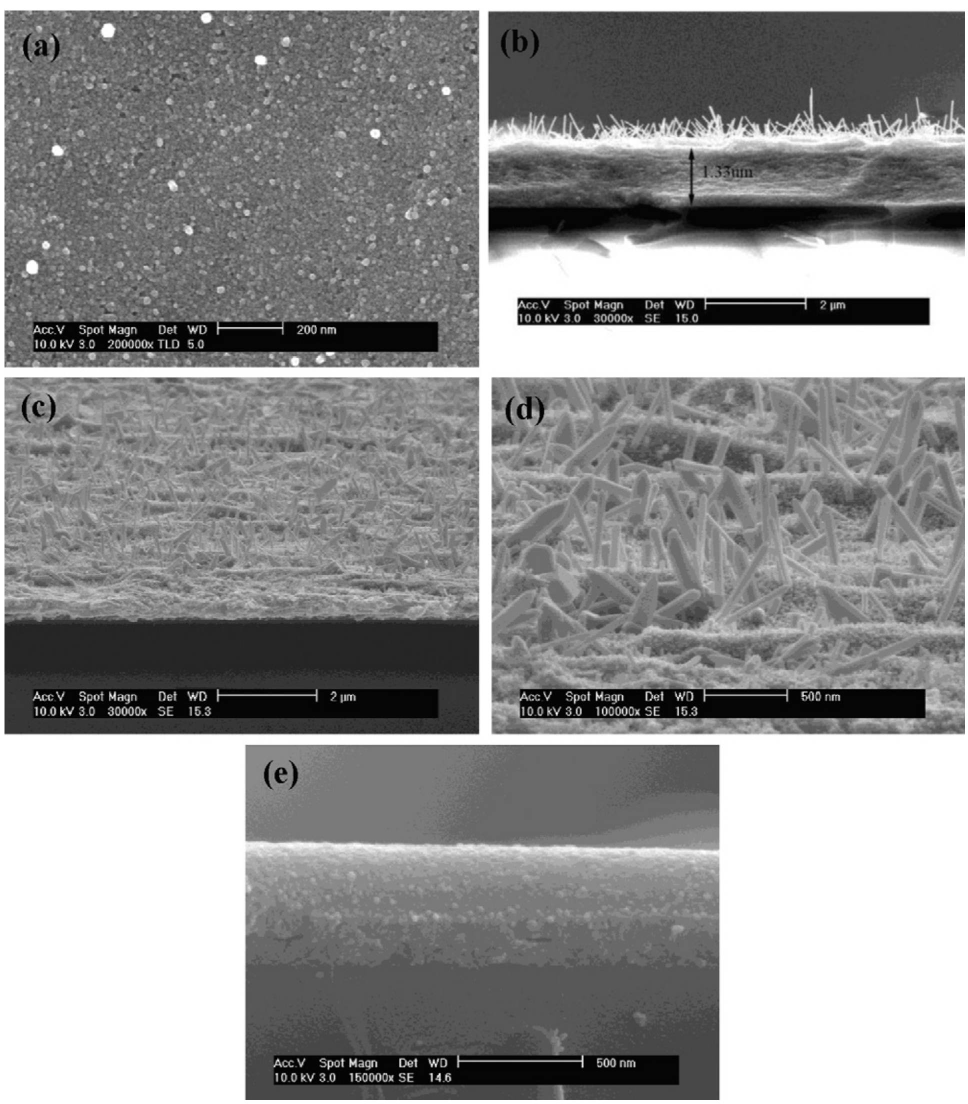

Fig. 2. Secondary electronic microscopy micrographs of 1.0 at% Al doped ZnO nanorods thin films annealed in hydrogen: (a) plane view, (b) cross-sectioned view, (c) and (d) cross-sectioned view with incident angle at 9°. (e) SEM micrographs of 1.0 at% Al doped ZnO thin films annealed in air: cross-sectioned view.