Journal of Alloys and Compounds 509 (2011) 3847–3851

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

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

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ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form
14 December 2010
Accepted 15 December 2010
Available online 23 December 2010

PACS:
81.07.−b
81.05.Dz

Keywords:
Al doped ZnO thin films
Nanorod
Annealed in hydrogen
Sol–gel spin-coating method
Optical and excellent electrical properties

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

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doi:10.1016/j.jallcom.2010.12.118

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

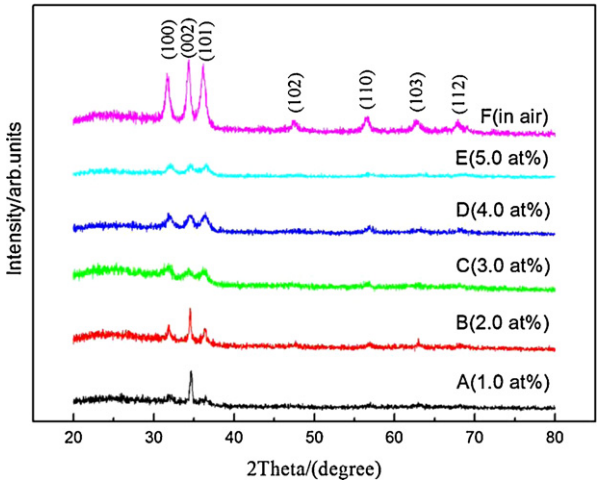

Fig. 1. X-ray diffraction patterns of the Al doped ZnO nanorods thin films.

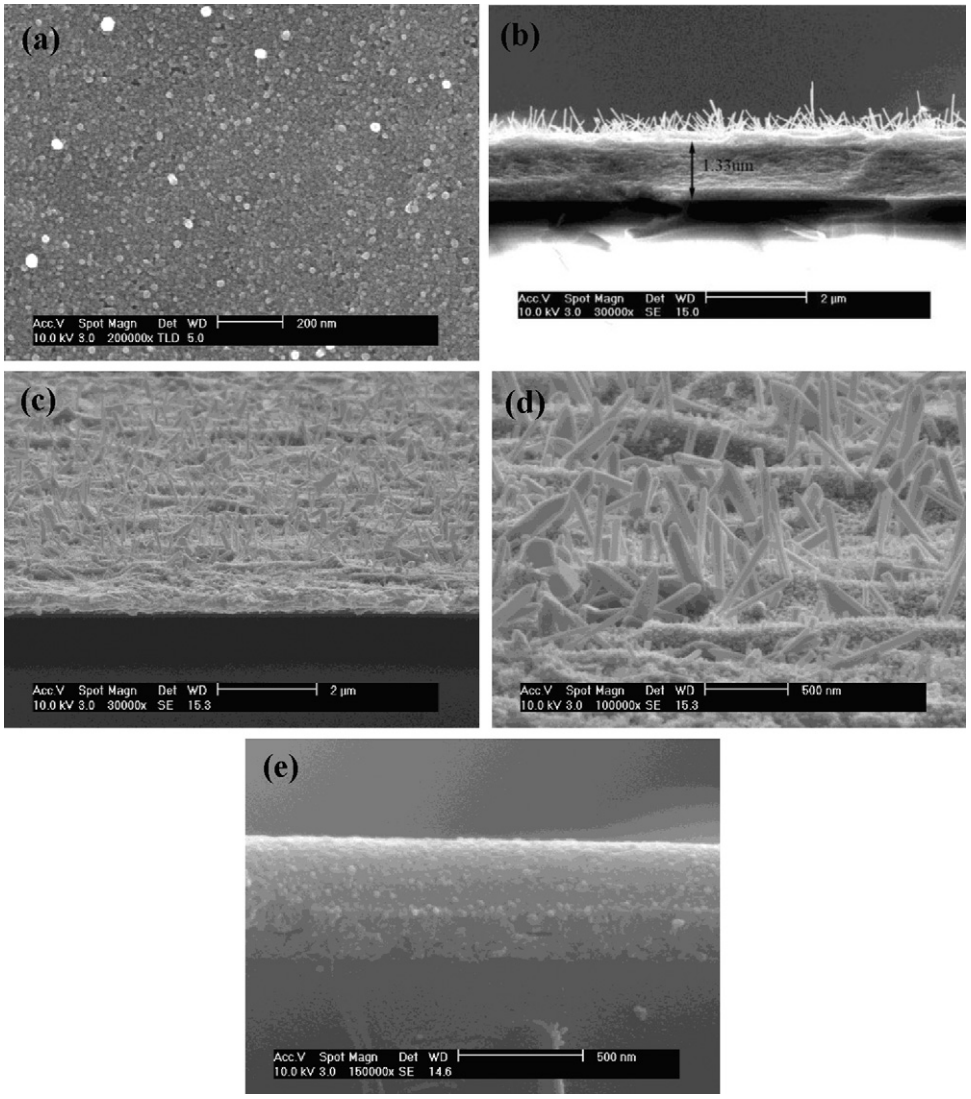

Fig. 2. Secondary electronic microscopy micrographs of 1.0 at% Al doped ZnO nanorods thin films annealed in hydrogen: (a) plane view, (b) cross-sectioned view, (c) and (d) cross-sectioned view with incident angle at 9°. (e) SEM micrographs of 1.0 at% Al doped ZnO thin films annealed in air: cross-sectioned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

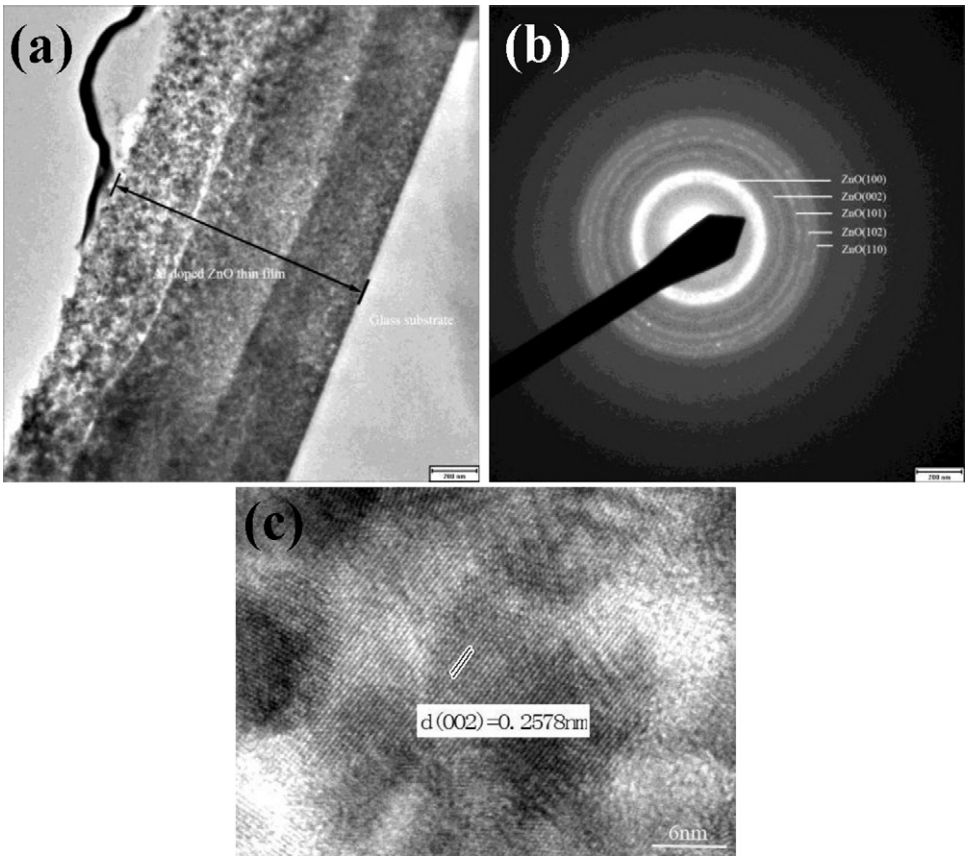

Fig. 3. Low-resolution cross sectional transmission electron microscopy image (a), selected-area electron diffraction pattern (b), high-resolution transmission electron microscopy image (c) of the 1.0 at% Al doped ZnO nanorod thin film.

of $a = 0.3249$ nm and $c = 0.5206$ nm, in good agreement with the literature of Ref. [15]. However, the (0 0 2) peaks of the diffraction patterns of ZnO films are quite different for different concentrations of Al, which indicates that the doping of Al has destroyed the crystal structure of ZnO thin films. The orientation of films is higher by annealing in hydrogen than in air. The higher intensity of the (0 0 2) diffraction peak indicates that the 1.0 at% Al doped ZnO nanorod thin films annealed in hydrogen are preferentially oriented in the *c*-axis direction.

In our experimental conditions, a novel one-dimensional nanostructure of ZnO nanorods with perfect hexagonal cross-section as building blocks for nanodevices is synthesized. The SEM micrographs of 1.0 at% Al doped ZnO nanorod thin films annealed in hydrogen are shown in Fig. 2(a)–(d). The cross-sectioned view of 1.0 at% Al doped ZnO nanorod thin film annealed in air is shown in Fig. 2(e), which suggests that the cross-sectioned plane is smooth. The overall morphology of the ZnO film deposited on a glass substrate is shown in Fig. 2(a). The cross-sectioned micrograph of the ZnO film is shown in Fig. 2(b), which shows the growth of ZnO naorods with average diameter of 45 nm and length of 366 nm at the ZnO film surface with the thickness of 1.33 μm. Fig. 2(c) and (d) are the cross-sectioned view of films with incident angle at 9°. The results indicate that the ZnO nanorod thin films can be got by annealing in hydrogen rather than in air.

Fig. 3(a) shows a low-resolution cross sectional TEM image of 1.0 at% Al doped thin film, annealed at 550 °C for 2 h in hydrogen. Which further demonstrates the result is that the surface of obtained sample is flat and the cross sectional plane is divided into three parts because the films were grown by three deposition/heat-treatment cycles. This is consistent with that of SEM photograph of samples. Fig. 3(c), the HRTEM image, shows clearly resolved lattice fringes and interplanar distance measured to be 0.2578 nm, which corresponds to the (0 0 2) plane of ZnO. The SAED pattern (Fig. 3(b)) of thin film is easily indexed on the basis of a hexagonal ZnO, which is in good agreement with the XRD pattern data.

3.2. Optical properties of ZnO thin film

Fig. 4 shows the transmittance spectra of the Al doped ZnO nanorod thin films with different concentrations, prepared on glass

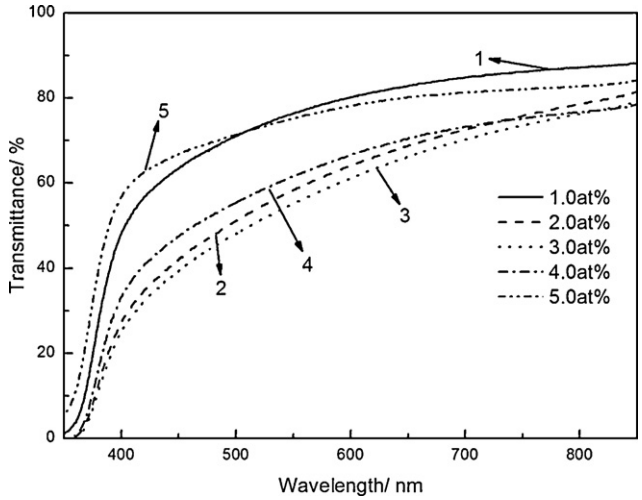

Fig. 4. Optical transmittance spectra of the ZnO thin films annealed in hydrogen with different concentrations of Al.

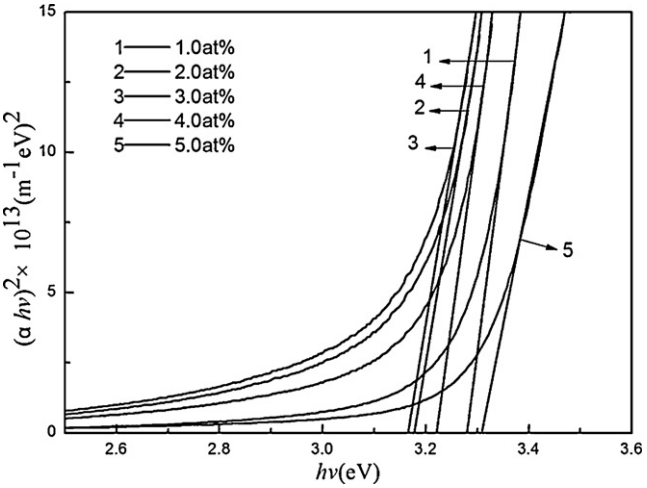

Fig. 5. Plots of $(\alpha h\nu)^2$ versus $h\nu$ of the ZnO thin films annealed in hydrogen with different concentrations of Al.

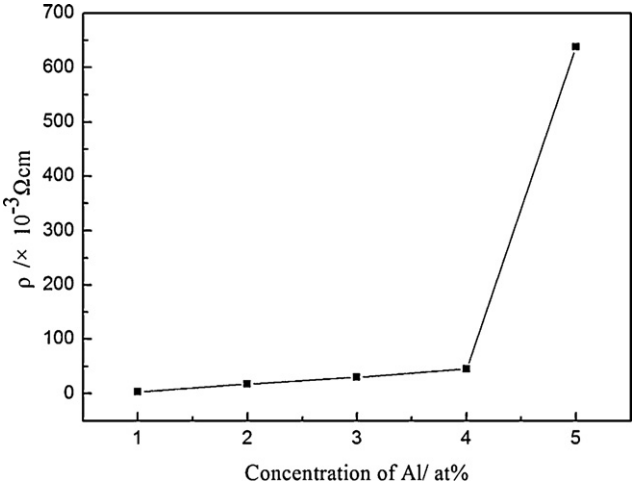

Fig. 6. Electrical resistivity of Al doped ZnO nanorods thin films.

substrates by sol–gel spin-coating method and annealed at 550 °C for 2 h in hydrogen. For all the films, they have high transmittances in the visible region and show sharp absorption edges in the UV region. The ZnO thin film doped with Al in a concentration of 1.0 at% has the highest transmittance in the visible region.

Optical band gap of the ZnO thin films can be obtained by applying the following two formulae (1) and (2): [16,17]

$$T = (1-R)^2\exp(-\alpha d), \quad (1)$$

$$\alpha h\nu = D(h\nu - E_g)^{1/2}. \quad (2)$$

in formula (1), T is the transmittance of the ZnO thin film, R is its reflectivity, α is the absorption coefficient, and d is the film thickness. In formula (2), $h\nu$ is the photon energy, D is a constant, and E_g is the optical band gap. According to formulae (1) and (2), we can calculate the absorption coefficient $\alpha \sim \ln T$ as well as $\alpha h\nu \sim (h\nu - E_g)^{1/2}$, as plotted in Fig. 5.

Fig. 5 shows the plot of $(\alpha h\nu)^2$ versus photon energy $(h\nu)$ obtained from the data of Fig. 4. Extrapolation of linear portion to the energy axis at $(\alpha h\nu)^2 = 0$ gives the E_g value. The E_g values obtained by the above process are 3.3, 3.2, 3.2, 3.2, and 3.3 eV, which are corresponding to the Al doped ZnO thin films with concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 at%, respectively. The band gap change depends on the electron concentration and hydrogenation [18]. Therefore, we conclude that the band gap change of ZnO films depends on the doping of Al and annealing in hydrogen.

3.3. Electrical properties of ZnO thin film

ZnO exhibits a wide range of conductivity and its behavior varies from metallic to insulating. The electrical characteristics can be controlled by doping with ternary elements or by adjusting process conditions [19]. The resistivity of the films is calculated from the following equation [20]:

$$\rho = \frac{\pi t}{\ln 2}\frac{V}{I}, \quad (4)$$

where t is the thickness of the sample, V is the voltage, and I is the current.

Fig. 6 shows the electrical resistivities of the Al doped ZnO thin films annealed in hydrogen with different concentrations of Al, which indicates that the resistivity of Al doped ZnO thin films annealed in hydrogen increases with the concentration of Al. We have also measured the 1.0 at% Al doped ZnO thin films annealed in air, which resistivity is of 73 Ω cm. The results indicate that 1.0 at% Al doped ZnO nanorod thin films annealed in hydrogen has a minimum resistivity of 3.2×10^{-3} Ω cm, which could be induced by the fine crystal structure that is preferentially oriented in the *c*-axis direction, suggesting that the orientation plays an important role in the conductivity of Al doped ZnO nanorods thin films. Oh et al. reported on the improvement of electrical property of ZnO thin films by annealing treatment in hydrogen [21]. They believe that reduced resistivity of the Al doped ZnO films is attributed to the increased free carrier concentrations and Hall mobility, which originated from the desorption of the negatively charged oxygen species from the grain boundary surfaces by the hydrogen treatment. Lee et al. [22] believe that treatment in hydrogen passivate the negatively charged oxygen species in the grain boundaries and the surfaces, which also act as carrier traps. Moreover, multicoordinated hydrogen also explains the dependence of electrical conductivity on oxygen partial pressure, resolving a long-standing controversy on the role of point defects in unintentional n-type conductivity of ZnO [23]. Therefore, we conclude that electrical characteristics of the Al doped ZnO nanorods thin films annealed in hydrogen were induced by the increased electron concentration and mobility due to the elimination of adsorbed oxygen species, excellent crystal structure, and multicoordinated hydrogen by the hydrogen-annealing treatment.

4. Conclusions

In summary, one-dimensional nanostructure of Al doped ZnO nanorods thin films were synthesized by the sol–gel spin-coating method on glass substrates annealed in hydrogen at 550 °C for 2 h. XRD analysis revealed that the Al doped ZnO nanorod thin films mainly consist of ZnO with wurtzite structure and shows the *c*-axis grain orientation. The optical properties reveal that the Al doped ZnO nanorod thin films annealed in hydrogen have an average transmittance of above 80% in the visible region and show sharp absorption edges in the UV region. The minimum resistivity reaches 3.2×10^{-5} Ω m when the ZnO nanorod thin film doping with the concentration of 1.0 at% Al and annealing in hydrogen at 550 °C for 2 h. This suggests that the Al doped ZnO thin films annealed in hydrogen have good crystal structure, and optical and excellent electrical properties.

Acknowledgements

The authors are grateful for financial support from the National 863 Program of China (2009AA03C116).

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