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Aluminum-doped zinc oxide thin film as seeds layer effects on the alignment of zinc oxide nanorods synthesized in the chemical bath deposition

Shengwen Hou, Chaoyang Li *

Nanotechnology Center, Research Institute, Kochi University of Technology, Kami City, Kochi 782-8502, Japan

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ABSTRACT

Aluminum-doped zinc oxide thin films with different thicknesses were deposited using a radio frequency sputtering system. As thickness increased, crystallinity improved and resistivity decreased. The optical transmittance of the films was over 80%. Well-aligned zinc oxide nanorods were synthesized on aluminum doped zinc oxide thin films in the chemical bath deposition. It was found that the morphological, structural, and optical properties of zinc oxide nanorods were significantly influenced by thicknesses of aluminum-doped zinc oxide films. Zinc oxide nanorods exhibited better crystallinity as film thickness increased. High transmittance of over 65% was obtained from zinc oxide nanorods. Vertical alignment of zinc oxide nanorods was dependent on growth direction of aluminum-doped zinc oxide films.

1. Introduction

Zinc oxide (ZnO) is one of the most promising semiconductors due to unique properties including direct wide band gap, large exciton binding energy, high mobility, and thermal stability [1,2]. ZnO has been widely applied in electronic and photonic applications including plasma displays, liquid crystal displays [3], ultraviolet laser diodes [4,5], dye-sensitized solar cells (DSSCs) [6], and sensors [7,8]. In order to apply ZnO in photovoltaic devices, ZnO nanorods should be fabricated on transparent conductive substrates [9]. Moreover, ZnO nanostructures with good alignment, large surface area and length-to-diameter ratio are very important to enhance performance in photovoltaics. The fabrication of ZnO nanorods on transparent conductive substrates as well as growth mechanism of ZnO nanorods has been reported in some studies [10–18]. Lee et al. [19] reported that ZnO nanorods could be synthesized on aluminum-doped ZnO (AZO) thin films for application in DSSCs. However, the morphology of ZnO nanorods could not be easily controlled. K. Nouneh et al. [20] compared the effects of substrates between AZO and indium-tin-oxide (ITO) seeds layers on morphology of ZnO nanorods. However, the mechanism that ZnO nanorods were well-aligned was not investigated in their study.

In order to fabricate well-aligned ZnO nanorods, a hybrid method combining both radio frequency (RF) magnetron sputtering method and chemical bath deposition (CBD) was presented. In our previous work, we had experience on controlling the properties of ZnO-related films deposited by RF sputtering system [21–23]. In addition, ZnO nanorods had been fabricated by the reducing annealing and CBD methods respectively [24,25]. However, some issues still remained on fabricating controllable ZnO nanorods. In this study, thickness dependence of AZO films on morphological, structural, and optical properties of ZnO nanorods was investigated in detail. The mechanism that ZnO nanorods were well-aligned was discussed.

2. Experimental procedure

2.1. AZO film deposition by RF magnetron sputtering

Alkali-free glass sheets (Eagle XG) were used as the substrates for deposition of AZO films. AZO films were deposited on the glass substrates in a conventional RF (13.56 MHz) magnetron sputtering system. A 4-inch AZO ($ZnO:Al_2O_3 = 98:2$ wt%) target was used in the sputtering system. The glass substrate was set 60 mm away from the target. During the sputtering process, pure argon (30 sccm) was introduced as the working gas. The pressure and the temperature were maintained at 1 Pa and 150 °C respectively. Controlling the deposition time, AZO films with different thicknesses (50, 100, 150, and 200 nm) were deposited.

2.2. ZnO nanorods fabricated by CBD method

After deposition, the obtained AZO films were used as substrates for growing ZnO nanorods. A mixed solution of $Zn(NO_3)_2 \cdot 6H_2O$ with a

* Corresponding author.

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concentration of 0.025 mol/L and hexamethylenetetramine (HMT) with a concentration of 0.0125 mol/L was prepared in a bottle, using ultrapure water as a solvent. The solution was transferred to a sealed flask as the reactor. The substrates were fixed vertically on a holder so that the substrate surfaces faced sideways in the solution. The flask was put in water and kept at 95 °C for 5 h. After the growth, the substrates were taken out of the solution and washed with ultrapure water in an ultrasonic cleaner several times, then air-dried at room temperature.

2.3. Characterization

Electrical property measurement were conducted with a Hall Effect system (Accent HL5500, M-1) at room temperature, using the Van der Pauw method to measure the type of carriers and the carrier concentration. Structural properties were measured with X-ray diffraction (Rigaku ATX-G diffractometer), which was operated in 2θ/ω sweeping from 20 to 40° in 2θ with a step width and a scan speed at 2°/min and employed Cu Kα tube (λ = 0.154178 nm) radiation with a power of 15 kW (50 kV, 300 mA). Morphological properties were examined using a field emission scanning electron microscope (FE-SEM) system (JEOL-JSM7400). The operating voltage was set at 5.0 kV. Transmittance was measured by means of a UV spectrophotometer (U-4100, Hitachi). A transmission electron microscope (TEM) system (JEOL-2100F) was employed to observe the microstructure of ZnO nanorods. The acceleration voltage was set at 200 kV. The photoluminescence spectra were taken using an iHR320 Micro-PL/Raman spectroscope (Horiba). A He–Cd laser with a wavelength of 325 nm in a power of 1 mW was used as the excitation light source. All measurement was carried out at room temperature.

3. Results and discussion

3.1. Electrical properties of AZO films

The as-deposited AZO films were investigated on their electrical properties in order to serve as the conductive substrates in photovoltaic fabrication. Fig. 1 showed the resistivity, mobility, and carrier concentration of AZO films as functions of film thickness. As the thickness of AZO film increased, the resistivity decreased significantly, while mobility increased and carrier concentration increased. The reason why carrier concentration in AZO films increased was because much more aluminum atoms were doped in AZO films, which introduced more free electrons for transportation.

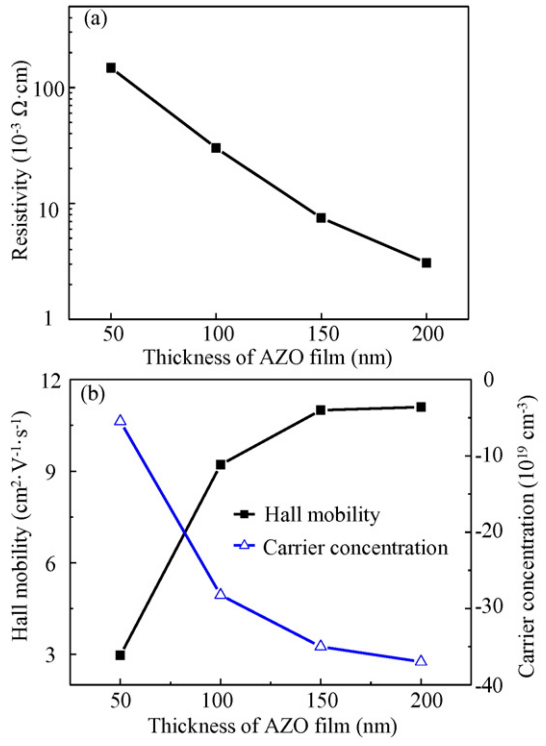

Fig. 1. (a) Resistivity, (b) hall mobility and carrier concentration of AZO films as functions of film thickness.

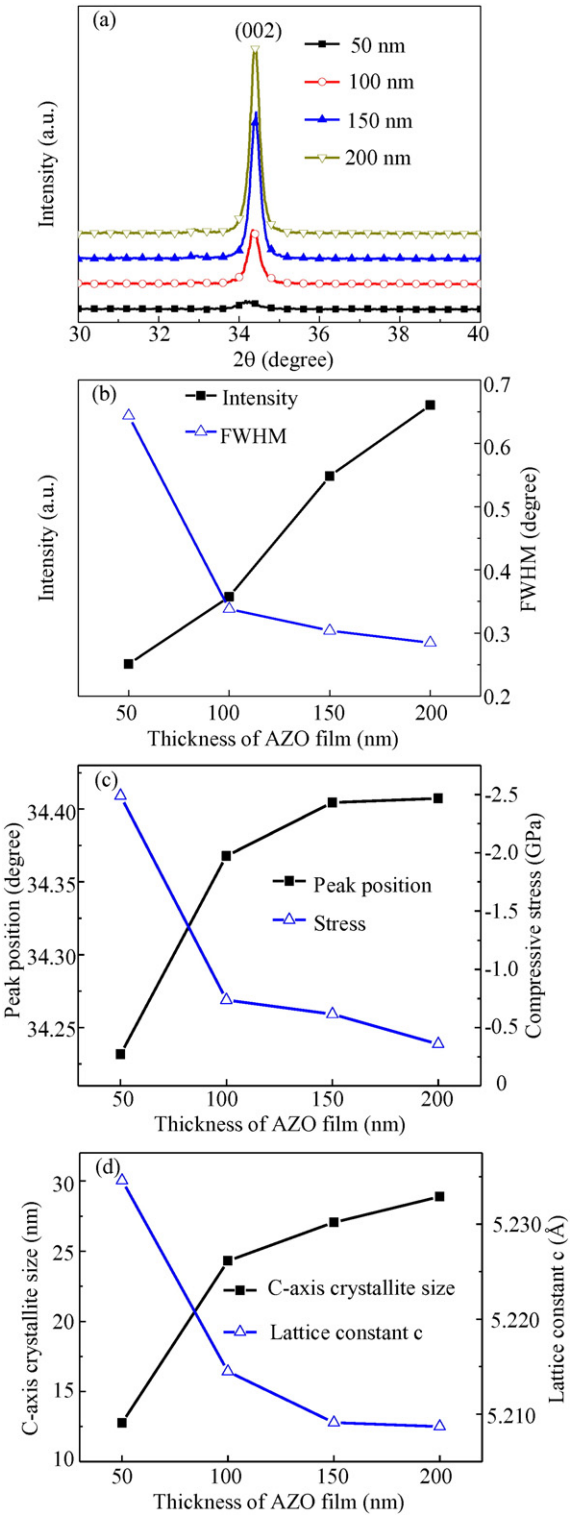

Fig. 2. (a) XRD patterns, (b) intensity and FWHM, (c) peak position and compressive stress, (d) c-axis crystallite size and lattice constant c of AZO films with different thicknesses.