Materials Science in Semiconductor Processing 16 (2013) 1316–1320

Contents lists available at SciVerse ScienceDirect

Materials Science in Semiconductor Processing

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

Vertically aligned ZnO nanowires prepared by thermal oxidation of RF magnetron sputtered metallic zinc films

Liang-Chiun Chao*, Sung-Yu Tsai, Ci-Neng Lin, Chung-Chi Liau, Ci-Chao Ye

Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

ARTICLE INFO

Available online 10 June 2013

Keywords:
Zinc oxide
Thermal oxidation
Field emission

ABSTRACT

ZnO nanowires have been successfully grown by thermal oxidation of metallic zinc films at 430 °C. Polycrystalline zinc films were deposited on Si (100) substrates by RF magnetron sputtering utilizing discharge power from 70 to 180 W. Experimental results show that 70 W discharge power results in the formation of porous zinc nanoparticles that prevent zinc atom from diffusion and thus does not result in the formation of ZnO nanowires by subsequent thermal oxidation. By increasing discharge power to 120 W the zinc film transforms to Zone II with a columnar structure, while further increase in discharge power to 180 W results in re-crystallization and formation of micron-sized hexagonal structures on the surface. Vertically aligned ZnO nanowires can only be obtained by thermal oxidation of columnar zinc films that exhibit a field emission threshold of 5.3 V/μm (at a current density of 10 μA/cm^2) with a field enhancement factor of 1834. A target current density of 0.75 mA/cm^2 is achieved with a bias field less than 10 V/μm.

1. Introduction

Low dimensional ZnO nanostructures are a promising candidate for next generation opto-electronic devices as ZnO nanostructures have found practical applications in ultraviolet nanolasers [1], cold field emitter [2] and chemical sensors [3]. One dimensional ZnO nanostructures have been prepared by chemical vapor deposition (CVD) [4], vapor phase transport [5] or by thermal oxidation of metallic zinc [6–12]. Preparation of ZnO nanowires by thermal oxidation is of great value due to its catalyst-free and low processing temperature (< 450 °C) characteristics. However, up to date, ZnO nanowires prepared by thermal oxidation of metallic zinc usually exhibit irregular-shaped island structures or wrinkled surface morphology [12] which is inappropriate for large scale flat panel display applications. RF magnetron sputtering is a convenient process for large area uniform thin film deposition. Zinc film deposited by RF magnetron sputtering may serve as a building block for the formation of ZnO nanowires for large scale field emission flat panel display application. By controlling RF discharge power, adatom energy is tuned so that zinc film with a different crystallinity may be achieved [13]. In this article, we report the effect of RF discharge power on the crystalline quality of zinc films. Effects of zinc film crystalline quality on the alignment of ZnO nanowires and its field emission properties are presented.

2. Experimental

Polycrystalline zinc films were deposited on Si (100) substrates at room temperature by the RF magnetron sputtering system utilizing metallic zinc (99.99%) targets. The distance from the substrate to the target was 55 mm and the working gas was argon (5 N). The base pressure

* Corresponding author. Tel.: +88 6227376369; fax: +88 6227376424.
E-mail addresses: lcchao@mail.ntust.edu.tw, lcchao@hotmail.com (L.-C. Chao).

1369-8001/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.mssp.2013.05.011

and working pressure were 4×10^{-6} Torr and 5×10^{-3} Torr, respectively. The RF discharge power was 70 W, 120 W, and 180 W and zinc films deposited under these conditions were referred to as Zn70, Zn120, and Zn180, respectively. A mechanical shutter was positioned between the target and the substrate to control the deposition time to 60 s. Metallic zinc targets were pre-sputtered while monitoring the emission spectra of the plasma. The shutter remains closed until the plasma emission line is dominated by zinc atomic ions. The as-deposited Zn70 sample exhibits a porous structure with a thickness of roughly 5 μm, while the as-deposited Zn120 and Zn180 are densely packed with thicknesses of approximately 2 μm and 4 μm, respectively. Zinc films were subsequently oxidized at 430 °C for 10–500 min in flowing oxygen (5 N) ambient. Surface morphology and crystallinity of as-deposited and annealed films were analyzed by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6500F, 15 keV) and x-ray diffraction (XRD, Bruker D2 Phaser diffractometer, Cu K_α, $\lambda = 0.15406$ nm), respectively. A transmission electron microscope (TEM, Philips Tecnai G2 F20) was employed to investigate the structural property of ZnO nanowires.

3. Results and discussion

Fig. 1 shows SEM micrographs of as-deposited and annealed Zn70, Zn120, and Zn180 samples. The annealing was performed at 430 °C in flowing oxygen ambient for three hours. The as-deposited Zn70 shows nanoparticles with the size of ~50 nm (Fig. 1a). As RF power increases to 120 W, closely packed randomly oriented hexagonal-shaped nanostructures were found across the wafer (Fig. 1b). As discharge power reaches 180 W, hexagonal shaped disk with the size of ~1 μm was found (Fig. 1c) instead. After oxidation, no ZnO nanowires were found on Zn70 (Fig. 1d), while vertically aligned ZnO nanowires can be found across the substrate of Zn120 (Fig. 1e). On Zn180 substrates, tilted ZnO nanowires and nanoclusters were found (Fig. 1f) instead. The change in zinc film crystallinity as RF discharge power increases is due to the further

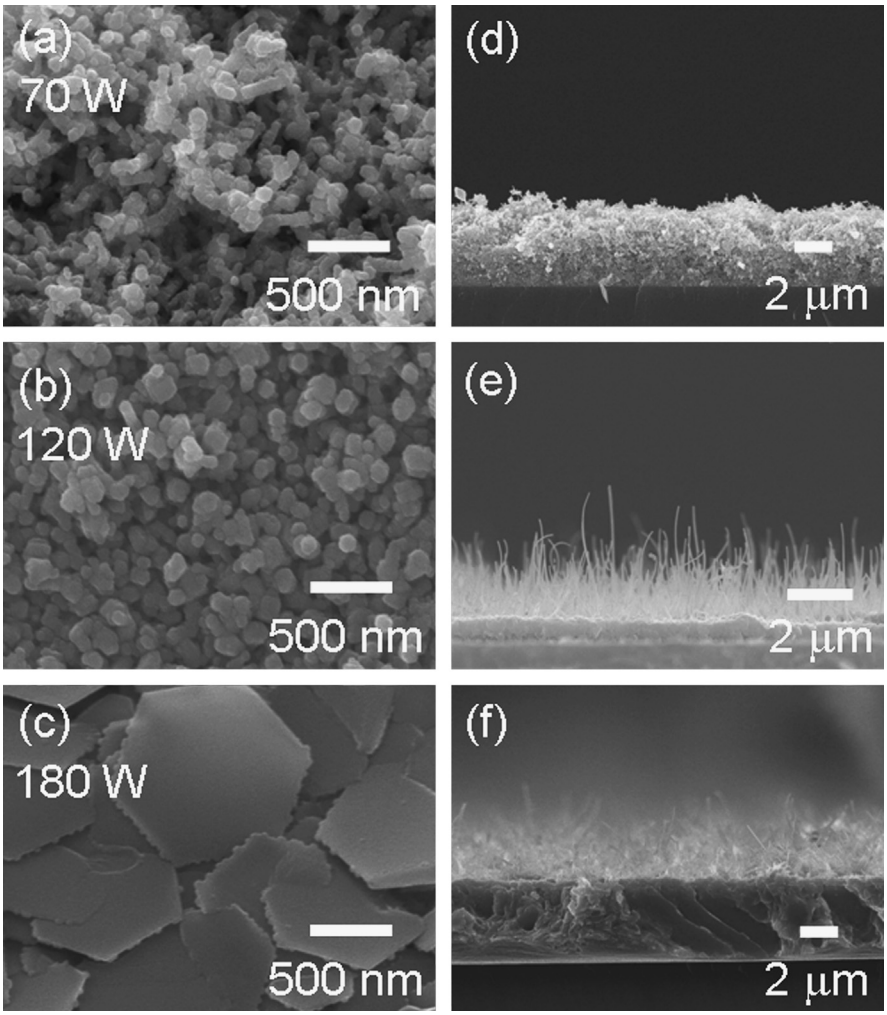

Fig. 1. FE-SEM micrographs of as-deposited (a) Zn70, (b) Zn120, and (c) Zn180, and annealed (d) Zn70, (e) Zn120, and (f) Zn180 films. The annealing was performed at 430 °C in flowing oxygen ambient for three hours.