Vacuum 155 (2018) 408–411

Contents lists available at ScienceDirect

Vacuum

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

Short communication

Enhancement of UV photoluminescence in ZnO tubes grown by metal organic chemical vapour deposition (MOCVD)

S. Iwan[a,*], J.L. Zhao[b], S.T. Tan[c], X.W. Sun[d]

[a] Program Studi Fisika, FMIPA Universitas Negeri Jakarta, Jalan Rawamangun Muka, Jakarta Timur, 13220, Indonesia
[b] NanoArc Technology Pte. Ltd., Singapore 389730, Singapore
[c] School of Electrical & Electronic Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore
[d] Department of Electrical and Electronic Engineering, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China

ARTICLE INFO

Keywords:
ZnO tubes
MOCVD
Growth temperature
Reactor pressure
Zn-O ratio

ABSTRACT

We have synthesized ZnO tubes, without any catalyst, on Al_2O_3 (001) substrates by metal organic chemical vapor deposition (MOCVD) at different growth temperatures, pressures and Zn-O ratios. The results confirm that the growth temperature, reactor pressure and Zn-O ratio play important roles in the formation of hexagonal ZnO tubes. Scanning electron microscopy (SEM) images indicated that, at a growth temperature of 500 °C, reactor pressure of 75 Torr and Zn-O ratio of 10/75 are an appropriate condition to obtain hexagonal and well-aligned ZnO tubes. High-resolution, double crystal XRD analysis shows a symmetric ω-scan rocking curve, with a full width at half maximum (FWHM) of 1.1°. It confirms the ZnO tubes have highly c-axis orientation on Al_2O_3 substrate. Subsequently, room temperature photoluminescence (PL) studies confirm that the enhancement of UV emissions from ZnO tubes is due to increasing Zn-O ratios.

1. Introduction

The invention of carbon nanotubes (CNTs) in 1991, by Ijima [1], has stimulated numerous efforts to study nanostructures. The nanostructures from various materials, such as BN, AlN, GaN, InN, Si, ZnO, etc, have been studied theoretically and experimentally [2]. Among these materials, the ZnO as a II-VI semiconductor, has potential applications for optoelectronics devices, due to a direct wide band gap (3.37eV) and large exciton binding energy (60 meV) at room temperature [3,4].

ZnO, with various kinds of nanostructures, has been synthesized with different methods, such as metal organic chemical vapor deposition (MOCVD) [5–7], wet chemical method [8], physical vapor deposition [9], hydrothermal [10,11] and solution-based method [12–14]. As compared to other methods, MOCVD offers better quality to obtain well-aligned ZnO nanostructure, due to well controlled, growth temperatures and reactor pressure [5,7,15]. Furthermore, an addition of a catalyst, or a template, is necessary to synthesize a certain ZnO nanostructure [16,17].

Recently, a low dimensional tubular structure of ZnO become a major interest because it has unique optical and electronic properties [12,14,18–20]. It also has high porosity and a large surface to volume ratio, which is needed to improve efficiency in microelectronic applications [7,21]. These properties bring ZnO nanotubes, without any dopants, and are a potential candidate for photo-electrochemical solar cells [17], photocatalyst [14,22,23], light emitting diode (LED) [24] and UV detectors [25]. Moreover, by using 3 d transition metal as a dopant, the ZnO nanotubes are believed to be potentially useful in applications of spintronics and nanomagnets [26]. Nevertheless, the orientation and controlled crystalline morphology, with a simple and rapid process, still remain a challenge [17,27]. Furthermore, the formation mechanism of ZnO nanotubes is still not clearly understood; meanwhile it's claimed, due to the Ehrlich-Schwoebel mechanism effect [28]. In 2016, A. Alshanableh et al. demonstrated the two step, facile hydrothermal and air-cooled hydrolysis method, which can be used to tune ZnO nanorods to twins nanotubes [10]. Meanwhile, B. Wang et al. reported that, based on density functional theory, the ZnO nanotubes were more stable than the graphitic phase [18].

In this paper, we report the fabrication of tubular ZnO, without any catalysts on a Al_2O_3 (001) substrate, by metal organic chemical vapor deposition (MOCVD) at different growth temperatures (450 °C, 475 °C, and 500 °C). The influence of growth temperatures, reactor pressures and II-VI ratios on morphology and photoluminescence properties of ZnO tubes will be discussed.

* Corresponding author.
E-mail addresses: iwan-sugihartono@unj.ac.id (S. Iwan), sunxw@sustc.edu.cn (X.W. Sun).

https://doi.org/10.1016/j.vacuum.2018.06.035
Received 27 March 2018; Received in revised form 12 June 2018; Accepted 12 June 2018

2. Experimental

The ZnO tubes were deposited on Al_2O_3 (001) substrate by using handmade metal organic chemical vapor deposition (MOCVD). Dimethylzinc (DMZn) and N_2 were used as precursor and carrier gas. High purified O_2 was used as an oxidizing agent. The DMZn bubbler was kept in a −5 °C anti-freeze water bath. The substrates were cleaned by an ultrasonic bath using acetone and ethanol, and then rinsed with de-ionized (DI) water, and then placed in the reactor chamber. The mass flow rate of DMZn was maintained at 10 standard cubic centimeters per minute (sccm). Meanwhile, the mass flow rate of O_2 varied 25, 50 and 75 standard cubic centimeters per minute (sccm). The growth pressure was varied from 25 to 75 Torr, and the growth temperatures were from 450 to 500 °C. Growth time was fixed at 25 min for each growth process. The surface morphology, crystal alignment and optical properties were examined using a scanning electron microscope (SEM), Philips X'pert diffractometer and Renishaw micro-PL system with a 325 nm He-Cd laser as the excitation source, respectively.

3. Results and discussion

Fig. 1(a–c) show SEM images of the ZnO rods and tubes at different growth temperatures under constant pressure (75 Torr) and II-VI (Zn-O) ratio (10/75). Fig. 1(a) shows the image of ZnO rods at the growth temperature of 450 °C. It can be seen from the figure that the diameter sizes of the ZnO rods at 450 °C are in the range of 50–200 nm. Meanwhile, Fig. 1(b and c) show the ZnO tubes, with the hexagonal shapes, formed at the temperature of 475 °C and 500 °C, with the outer diameter in the range of 200–250 nm and 300–500 nm, respectively. According to SEM images, as shown in Fig. 1(a–c), it can be clearly seen that the density of ZnO tubes at the growth temperature of 500 °C is higher. On the other hand, the hexagonal ZnO tubes with outside diameter 0.4, 0.7, 1 μm can be epitaxially formed on sapphire (001) substrates by MOCVD, without any catalyst for growth at temperatures of 450, 425, 350 °C, respectively [5]. Furthermore, at 500 °C, no tubular ZnO can be obtained [5]. Meanwhile, ZnO tubes with diameter ranges of 10–15 nm can be obtained by decreasing growth temperature from 650 °C to 450 °C under a constant reactor pressure of 10 Torr [7].

Fig. 1(d–f) show the morphology of ZnO structures under various reactor pressures when growth temperature and Zn-O ratio were maintained at 500 °C and 10/75, respectively. As seen in the figure, the improvement of ZnO tubes depends on the increasing reactor pressure. The tubular ZnO structure can be observed when the growth temperature and Zn-O ratio was maintained at 500 °C and 10/75, respectively. Under reactor pressure of 25 Torr, the vertical and irregular graphitic phases are dominant on the sample surface. Furthermore, the formation of tubular phases was observed clearly under 50 Torr. Meanwhile, the formation of hexagonal ZnO tubes with vertical alignment was obtained under the reactor pressure of 75 Torr. It means that the optimum ZnO tubes with the hexagonal shapes can be formed at the reactor pressure of 75 Torr. This result is quite surprising, since others reported that ZnO nanotubes can be formed by decreasing growth pressure from 10 to 0.06 Torr [29].

In addition to the growth temperature and reactor pressure [5,7], we believed the ratio of Zn/O was also a very important factor to form ZnO tubes. Fig. 1(g–i) show the SEM images of ZnO tubes grown at 500 °C and constant pressure (75 Torr) with different Zn-O ratios (10/25, 10/50, and 10/75). Interestingly, there are spiral column shapes observed from SEM images (Fig. 1(g)). This indicates that there are graphitic phases of ZnO. Meanwhile, Fig. 1(h) shows the ZnO tubes with irregular shapes. It's predicted that by increasing the Zn-O ratio, the formation of ZnO tubes is optimum. As seen in Fig. 1(i), the ZnO tubes have a more regular shape with a larger diameter. Meanwhile, the graphitic phase diminished. The formation of tubular ZnO is related to the different growth rate of the various crystal facets and the polar (0001) surface [30,31]. Therefore, we believe it was influenced by the

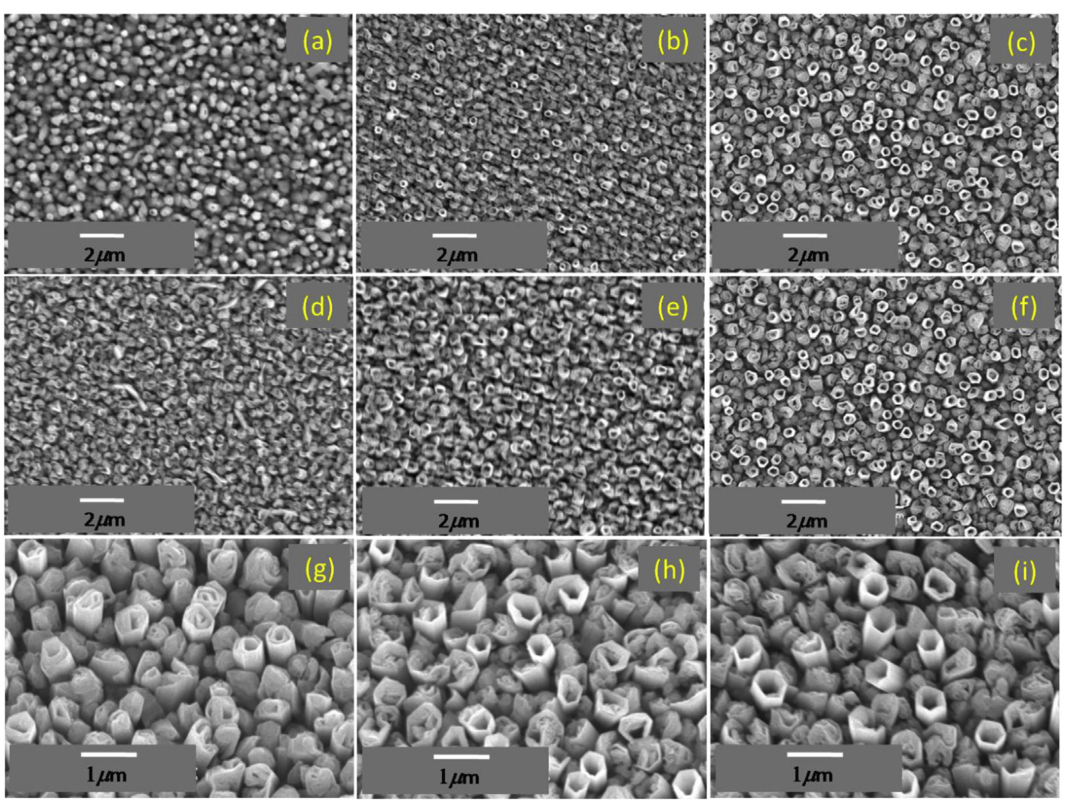

Fig. 1. SEM images of the top of ZnO rods and tubes: (a–c) different growth temperatures under a constant pressure of 75 Torr and the Zn-O ratio of 10/75. (a) 450 °C, (b) 475 °C, (c) 500 °C; (d–f) SEM images of the top of ZnO tubes with various reactor pressureat 500 °C and the Zn-O ratio of 10/75. (d) 25 Torr, (e) 50 Torr, (f) 75 Torr; (g–i) SEM images of the top of ZnO tubes with a various Zn-O ratio at 500 °C and a constant pressure of 75 Torr. (g) 10/25, (h) 10/50, (i) 10/75.