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

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Abstract

We have synthesized ZnO tubes, without any catalyst, on Al2O3 (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 c-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 Al2O3 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 Iijima [1], has stimulated numerous efforts to study nanomaterials. The nanomaterials 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 due to a direct wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [3,4].

ZnO, with various kinds of nanomaterials, 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 nanomaterials, 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 nanomaterial [16,17].

Recently, a low dimensional tubular structure of ZnO become a major interest because it has unique optical and electronic properties [12,14,16-20]. It also has high porosity and a large surface to volume ratio, which is needed to improve efficiency in microelectronic applications [17,21]. 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. Absharabilotha 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 graphene phase [18].

In this paper, we report the fabrication of tubular ZnO, without any catalysts on an Al2O3 (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 in morphology and photoluminescence properties of ZnO nanotubes will be discussed.

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

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
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appropriate environment during the growth process. Under the oxygen-rich condition, the density of Zn ions around ZnO rods during growth processes were higher than the top surfaces [32]. Consequently, the reaction rates of Zn and O ions at the top edges and side walls of the ZnO rods are higher than at the center. As a result, the ZnO tubes are produced along the c-axis. B.P. Zhang et al. suggested that the formation of ZnO tubes originated from spiral column growth [5]. Meanwhile, the tubular form of ZnO, formed under appropriate conditions, resulted in a coalescence of the graphitic phase [18].

Fig. 2 shows the XRD pattern of hexagonal ZnO tubes with ZnO ratio, growth temperature and pressures that are 10/75, 500 °C and 75 Torr, respectively. Inset of the figure shows the rocking curve of ZnO (002) planes, with the full width at half maximum (FWHM), which is 1.1°. It indicates that the ZnO tubes have a hexagonal c-axis orientation on Al2O3 substrate.

We further investigated room temperature photoluminescence (PL) and properties of ZnO tubes, which are influenced by growth temperature of 500 °C, reactor pressure of 75 Torr and the ZnO ratio of 10/75. As seen in Fig. 3, room temperature PL spectra of ZnO tubes for all ZnO ratios has, typically, two emissions, i.e. ultraviolet (UV) and green band (GB). Inset of the figure shows an inclination angle of the SEM image of the ZnO tubes at 500 °C and under 75 Torr and the ZnO ratio of 10/75. The PL spectra show the excitonic-related UV emissions (~380 nm), which represent near band edge (NBE) emission [33]. Meanwhile, the defect-related GB (visible) emission (~600 nm) represents deep level emission (DLE) [10]. All the observed peaks confirm that the ZnO tubes have strong UV emissions that correspond to the recombination of free excitons. Moreover, the UV intensity of ZnO tubes increased by increasing oxygen conditions. It indicates that the crystalline quality of ZnO tubes improved significantly when the Zn to O ratio is 10/75. According to our previous reports, the UV/GB ratio is used to evaluate the existence of native defects in ZnO structure [34]. It can be seen that the PL spectrum of ZnO ratio of 10/75 has the UV/GB ratio of 9.28, which is higher than other ratios (4.45 and 4.43). Hence, we believe growth processes of ZnO tubes under oxygen-rich conditions can reduce some common defects, such as oxygen vacancies. Consequently, the crystal quality of ZnO tubes improved. According to our results, the improvement crystal quality of ZnO tubes can be identified by the enhancement of UV emissions. It is also reported by Zeng et al. that oxygen ambient could remove the defects, such as excess zinc or oxygen vacancy [35]. Nevertheless, we observed some other defects, such as interstitial zinc (Zni), zinc vacancy (Vzn) and oxygen interstitial (Oi) which all still lie on the ZnO structure.

Hence, we conclude that the optimum formation of ZnO tubes can be obtained under an ideal environment, i.e. growth temperature of 500 °C, reactor pressure of 75 Torr and the ZnO ratio of 10/75. As reported in the last decade by B.P. Zhang et al. we also believe that ZnO tubes have potential applications as UV lasers and field emission devices [29].

4. Conclusions

In conclusions, we have successfully synthesized ZnO tubes by MOCVD at different growth temperatures, pressures and ZnO ratios. The results indicate that the highly c-axis oriented ZnO tubes can be obtained by controlling the growth temperature of 500 °C, reactor pressure of 75 Torr and the ZnO ratio of 10/75. The room temperature PL spectrum of ZnO tubes shows the UV enhancement by increasing the ZnO ratio. It is predicted that the crystalline improvement of ZnO tubes can be obtained under oxygen-rich environments in certain growth and reactor pressure conditions.

Acknowledgments

XW Sun would like to thank the support from the National Key Research and Development Program of China administrated by the Ministry of Science and Technology of China (No. 2016YFA0401702), National Natural Science Foundation of China (No. 61674074), Shenzhen Peacock Team Project (No. KQTD201603011203005), Shenzhen Innovation Project (No. JCYJ2016030113356947, and JCYJ2016030113357474), and the start-up fund from Southern University of Science and Technology.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.vacuum.2018.06.035.

References
