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Growth mechanism of seed/catalyst-free zinc oxide nanowire balls using intermittently pumped carrier gas: Synthesis, characterization and applications

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ABSTRACT

We report the growth mechanism of ZnO nanowire balls by thermal evaporation under intermittently pumped carrier gas as a new and simple nucleation method. The structural, morphological, and optical properties of the nanowires were analyzed by field emission scanning electron microscopy, X-ray diffraction, UV–vis spectroscopy, and photoluminescence spectroscopy. Results showed that the proposed method facilitates epitaxial nucleation and growth of high density vertically aligned ZnO nanowires with length of several micrometers and that have a smaller diameter compared to that of ZnO nanowires fabricated by traditional continuous pumping described in the literature under the same growth condition. These findings suggest that the use of intermittently pumped carrier gas is one of effective control parameters that promote the nucleation and growth of nanomaterials using thermal evaporation method.

1. Introduction

Zinc oxide (ZnO) is an n-type II–VI wurtzite semiconductor with a wide direct band gap of 3.7 eV and an excitation binding energy of 60 meV. ZnO is a highly attractive material due to its availability, ease of fabrication, non-toxicity, low cost, and high transmittance in visible region, etc. [1]. One-dimensional (1D) nanostructure ZnO in the form of nanowires (ZnO-NWs) is very desirable in many important practical applications and is extensively studied because of its geometrical configuration, electron confinement properties, large surface-to-volume ratio, and polar nature [2].

Several chemical and physical methods are used to grow different types of ZnO-NWs. Among these methods, thermal evaporation is one of the conventional physical vapor depositions (PVD) methods. This method provides another commonly used methodology for synthesizing 1D nanostructures. The main features of this method are the possibility of producing different morphologies; the high-quality, cheap deposition systems; and the ease of controlling the growth rate and dimensions [3]. Numerous conditions can significantly affect the controlled synthesis of semiconductor materials using thermal evaporation method, such as growth temperature, growth time, kinds of substrates, glancing angle deposition, source material, and carrier gas [4–6].

Among these parameters, carrier gas is one of effective control parameters that promote the nucleation and growth of nanostructures, where the source materials can be vaporized at high temperature and then carried down by inert gas carrier to low-temperature regions. The vapor gradually becomes supersaturated. Once it reaches the substrate, nucleation and growth of nanostructures will occur [7,8]. Consequently, the carrier gas significantly affects the morphological, structural, and optical properties of nanostructures [9,10]. Recently, efforts have been devoted to fabrication of nanostructured materials by controlling the carrier gas. For example, Leung et al. [11] reported ZnO nanowires grown using different carrier gases (Ar, N_2, humidified Ar, and humidified N_2). In this research, type of carrier gas significantly affects the growth rate and optical properties of fabricated nanowires. Fangfang et al. [12] reported fabricating ZnO nanorods using different Ar carrier gas flux. In this study, the diameter of nanorods changed from 150 nm to 20 nm by changing carrier gas flux during the growth process. Wang et al. [13] reported ZnO films were grown using H_2 and He as carrier gases. ZnO films grown with He carrier gas showed improved crystallinity, smooth surface, and reduced

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defects concentration, as well as the film growth rate also increased. Bao et al. [14] reported effects of H_2 flow rate on AlN and AlGaN growth. In this research, both AlN and AlGaN growth rates increased as H_2 flow rate increased. Dhayalan et al. [15] reported the epitaxial growth of Si:C and Si:C:P layers using N_2 and H_2 as carrier gases. In this research, the N_2 instead of H_2 resulted in an increase of the growth rate and the surface defect density reduced. Cao et al. [16] reported that MoS_2 flakes grown on SiO_2/Si substrate using different Ar flow rates. In this study, the carrier gas flow rate has a strong influence on the morphology and structure of grown MoS_2 flakes.

In general, the controlled synthesis of nanostructures is a promising candidate that plays a vital role in the potential applications because the evolution of the morphology of films have a significant effect on the performance of functional surfaces by adopting a larger area, and mass-production-compatible methods remain a challenge. The growth of ZnO-NWs has been extensively studied to produce specific shapes, sizes, and surface densities because of the great influence in their potential applications [17]. The large aspect ratio and subwavelength diameter of nanowires have superior optical and electrical properties such as optical anisotropy and surface band bending [18,19]. Moreover, success in various applications requires the definition and control of the size and geometry of the nanostructures. Consequently, establishing the ability to customize the growth of ZnO-NWs to produce specified surface densities, sizes, and orientation is necessary for many applications such as light-emitting diodes (LEDs) [20], solar cells [21], photocatalyst [22], high volume production of electrodes for batteries [23], and UV photodetectors [24].

Among these nano-devices, ultraviolet (UV) photodetectors (PDs) have attracted significant attention in the past few decades because of their applications in various fields such as water purification, chemical analysis, remote control, solar astronomy, and biological sensing [25,26]. The UV detector based on the ZnO has attracted greater interest than those fabricated from other semiconductors such as AlGaN, SiC, and Si [27,28]. However, UV detectors based on ZnO-NWs have a long recovery time in the second scale because of the oxygen-related hole-trap states at the ZnO-NWs surface [29,30]. Therefore, many researchers have been focusing on fabricating UV detectors based on 1D ZnO-NWs, exerting significant efforts to enhance the response speed. For example, Zhou et al. [31] reported the possibility of reducing the recovery time from 417 s to 0.8 s using a Schottky contact instead of an ohmic contact in UV photodetector device fabrication. Prades et al. [32] reported that the surface coating of polymer can reduce the response time of photodetector ZnO-NWs. Recently, Yan et al. [33] reported that the UV photodetector based on Zn_2GeO_4-NW networks lead to the promotion of response speed because of the NW—NW- barrier- dominated conductance.

In an effort to achieve an effective route towards enhancement of nucleation and growth of nanomaterials, which in turn leads to large surface-to-volume ratio and high crystal quality, thereby improving the performance of UV photodetectors, this research focused on the carrier gas pumping method and its effect on the morphological, structural, and optical properties of ZnO NWs. Specifically, two ZnO films were subjected to carrier gas pumping under two different methods: one nanowire film was grown under intermittently pumped carrier gas as a new and simple nucleation method and the other by traditional continuous pumping under the same growth condition [34,35]. The field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), and photoluminescence spectroscopy studies indicate that the intermittently pumped carrier gas method facilitates epitaxial growth of higher density vertically-aligned ZnO-NWs with length of several micrometers, smaller diameter, higher crystallization and optical transparency in the visible region. Similarly, the fabricated UV photodetector based on ZnO-NWs prepared using the proposed method showed excellent stability over time, low dark current, high sensitivity, and good ability to respond due to the large length-to-diameter ratio of nanowires and high crystal quality. This study aims to use intermittently pumped carrier gas as a new method for synthesizing ZnO-NWs using thermal evaporation method, which will serve as a basis for further research to control the growth of different types of nanomaterials using thermal evaporation method.

2. Experimental details

ZnO-NW balls were grown on ITO seed layer coated glass substrate by thermal evaporation method in a horizontal tube furnace system. The seed layer of ITO were prepared by radio frequency (RF) reactive magnetron sputtering onto glass substrate, with a thickness of around 75 ± 5 nm. Prior to growth ZnO-NWs, the ITO seeds were annealed using a continuous wave (CW) CO_2 laser at temperatures of 450 °C in the air for 15 min, in accordance with our previous study [36]. High-purity metallic Zn powder (99.99%, Sigma-aldrich, USA) as a first source material loaded into a quartz boat. This boat with Zn powder was transferred into the center of the furnace using a quartz tube. The ITO seeds/glass substrate was placed horizontally in the downstream direction of the Zn material. Then, the Zn powder in the first zone was gradually heated up from room temperature to 650 °C at a rate of 10 °C/min, while the temperature of the glass substrate zone was at 425 °C. Upon arrival at the temperature of 450 °C, high-purity Ar gas as a carrier gas was fed intermittently at a rate of approximately 40 mL/min; an average of one every minute being fed in followed by a five minute stop. This process was repeated approximately 5 times, and then the Ar gas was fed continuously into the reaction zone at a rate of approximately 20 mL/min. High-purity O_2 gas was fed into the reaction zone at a rate of approximately 5 mL/min after the temperature reached 650 °C. Pumping of O_2 gas into the system continued for 60 min. A white material formed on the ITO seeds/glass substrate after evaporation was completed. Then, quartz tube was allowed to cool down naturally.

The surface morphology of the fabricated ZnO-NWs was analyzed using Carl Zeiss FESEM Leo-Supra 50VP equipped. The structure analysis was characterized through XRD PANalytical X'Pert PRO MRD- PW3040 with Cu-Kα radiation ($\lambda = 1.5418$ Å). The transmission curves were obtained by using a spectrophotometer kind; a Varian- Cary system 5000 UV—vis-NIR to determine the optical transmission spectra. The optical properties were measured using PL spectroscopy system (Jobin Yvon HR 800 UV, Edison, NJ, USA) with a He—Cd laser (325 nm, 20 mW).

3. Result and discussions

3.1. FESEM analysis

The morphologies of the ZnO-NW balls grown on ITO seed/glass substrate via thermal evaporation method using intermittently pumped carrier gas was measured by FESEM. Fig. 1(a) shows high magnification images of the large-scale micro uniform and the formation of highly dense of ZnO balls on the glass substrate. Fig. 1(b) shows low magnification images of the ZnO-NW balls, it can be seen that the nanowires of the ZnO balls grown as a radial morphology disperse, homogeneously on the substrate and are highly dense. The cross sectional view in Fig. 1(c) shows that the nanowires of the same sample grow quasi-vertically and are closely packed on the ITO seed layer with high growth rates of up to 20 μm. The nanowires have a diameter of approximately 60 nm.