Catalyst-Free Growth Of ZnO Nanowire Balls On ITO Seeds/Glass By Thermal Evaporation

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Abstract

A seed/catalyst-free growth of ZnO nanowire balls on ITO seed layer coated glass substrate by thermal evaporation was successfully fabricated by using an intermittently pumped carrier gas. These ZnO balls were grown on sputtered ITO seeds that were deposited on glass substrates by RF magnetron sputtering. The sputtered ITO seed layer was annealed using the continuous wave (CW) CO2 laser at 450 °C in air for 15 min. Studies were carried out on ZnO balls using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and UV-Vis spectrophotometer. The results showed good quality of ZnO balls with high growth rate could reach a length of 20 μm with diameter of 60 nm. The result in the present study suggests that the morphology control of nanostructures is important to enhance the efficient nanodevices for various applications.

Keywords: Nanostructures; Laser annealing; Vapor deposition; Optical properties.

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 deposition (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]. The controlled growth 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 [4]. In addition, the large aspect ratio and subwavelength diameter of nanowires have superior optical and electrical properties such as optical anisotropy and surface band bending [5,6]. 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) [7], solar cells [8], photocatalyst [9], high volume production of electrodes for batteries [10], and UV photodetectors [11]. In the present study, the growth of ZnO-NW balls on glass substrates by thermal evaporation method was successfully conducted for the first time with intermittently pumped carrier gas, instead of the traditional method of continuously pumped. This process allows the control of the nucleation process and hence the growth of the nanostructures, which serve as a basis for further research on the growth of nanostructures.

2. Experimental

ZnO-NWs were grown on ITO seed layer coated glass substrate by thermal evaporation method in a horizontal two-zone tube furnace. The seed layers of ITO were prepared by a radio frequency (RF) reactive magnetron sputtering onto glass substrate, with a thickness of around 75 ± 5 nm. Prior to growth ZnONWs, the ITO seeds were annealed using a continuous wave (CW) CO2 laser at temperatures of 450 °C in the air for 15 min, in accordance with our previous study [12]. 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 seed coated 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 melting point of Zn (419 °C), high-purity Argon gas as a carrier gas zone was fed intermittently at an average of one every minute being fed in followed by a five minute stop. This process was repeated approximately 5 times. 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 seed coated 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 melting point of Zn (419°C), high-purity Argon gas as a carrier gas zone was fed intermittently at an average of one every minute being fed in followed by a five minute stop. This process was repeated approximately 5 times. Subsequently, high purity Oxygen gas and the carrier gas (Ar gas) were fed continuously into the reaction zone and this was continued for 90 min. White material was formed on the substrate after the evaporation process was completed. The quartz tube was cooled naturally to room temperature. The surface morphology of the fabricated ZnO-NWs balls was analysed using Carl Zeiss field emission scanning electron microscope (FESEM) Leo-Supra 50VP equipped. The structure analysis was characterized through X-ray diffraction (XRD) PANalytical X’Pert PRO MRD- PW3040 with Cu-Kα radiation (λ=1.5418 Å). The optical transmission and absorption was studied using UV–vis–NIR spectrophotometer (Cary system 5000). The optical properties were measured using PL spectroscopy system (Jobin Yvon HR 800 UV, Edison, NJ, USA) with a He–Cd laser (325 nm, 20mW).

3. Results And Discussion

3.1 FESEM analysis

The morphologies of the ZnO-NW balls grown on ITO seeds/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-NW on the glass substrate. Fig. 1(b) shows low magnification images of the ZnO 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. Fig. 1(c) shows the EDX spectra of ZnO-NW which indicated the presence of Zn and O atoms in addition to In and Sn atoms of ITO seeds. The EDX appears that this sample contains 48.62 At.% Zn, 49.51 At.% O, 1.68 At.% In, and 0.19 At.% Sn, as shown in the table inset of Fig. 1(d). These ratios indicate good stoichiometry of the synthesized sample.

Figure 1 The top images, low and high magnification (a,b) and cross-sectional. (c) A typical EDX spectrum of ZnO balls

3.2 XRD study

Fig. 2 shows the XRD pattern of the ZnO-NW balls grown on ITO/glass substrates. Apart from the diffraction peaks of ITO seed layer, all peaks of the sample could be indexed to the hexagonal phase with a wurtzite structure of ZnO, according to ICSD 01-089-1397. The high and sharp diffraction peak of (002) direction indicates ZnO balls grow along the c-axis direction. An extensive XRD pattern of ZnO film appeared extending from 31.67° to 72.21° in the 2θ region, because this is typical of diffraction patterns for a glass substrate [13].

Figure 2 XRD pattern of ZnO-NW balls grown on glass substrate
3.3 Optical properties

Fig. 3 shows the UV–vis optical transmission spectra of the growth of ZnO-NW balls in a wavelength range of 200-800 nm, and the absorption spectra of the sample (inset of Fig. 3). The average optical transmission in visible light region is estimated to be 89.64%. The high transmittance of this sample in the visible light range is one of the essential factors for UV PDs, which indicates the high homogeneity and low surface roughness [14]. The inset shows the sharp absorption shoulder in the wavelength 300–400 nm (UV region); due to the quantum confinement effect of the ZnO balls.

![UV–vis transmission of the ZnO-NW balls film. The absorption for the sample is shown in the inset](image)

**Figure 3** UV–vis transmission of the ZnO-NW balls film. The absorption for the sample is shown in the inset

3.2 XRD study

Fig. 4 shows the room temperature PL spectra of the ZnO-NW balls on ITO seeds/glass substrates by thermal evaporation using carrier gas feeding intermittently. The PL spectra of the film was excited by a He–Cd laser (λ= 325 nm). The spectra exhibited one strong UV emission peak a near band edge (NBE) emission (UV region) at 378.2 nm, which is similar to the results reported by Fang et al. [15]. This peak can be attributed to the recombination of the excitons through an exciton–exciton collision process [16]. In the visible region, ZnO balls demonstrated a weak broad deep level emission (DLE) at 513 nm. This emission is a result of the sub-band transition that appeared to be intrinsic in the nanostructure [17].
4. Conclusion

This work proposed the fabrication of ZnO-NW balls on ITO seeds-coated glass substrate by a thermal evaporation under intermittently pumped carrier gas as a new nucleation method, which will serve as a basis for further research to control growth of nanomaterial using thermal evaporation method. The results showed that compared with a previous study using traditional continuous pumping, the nanowires of ZnO balls have a higher density with vertical growth and that the growth rate can reach a length of 20 μm, a diameter of 60 nm, as well as higher crystallization and optical transparency in the visible region.

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6. References


