Journal of Alloys and Compounds 660 (2016) 480–485

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Confocal electroluminescence investigations of highly efficient green InGaN LED via ZnO nanorods

Hyun Jeong [a], Mun Seok Jeong [a, b, *]

[a] Center for Integrated Nanostructure Physics, Institute for Basic Science, Sungkyunkwan University, Suwon, 440-746, Republic of Korea
[b] Department of Energy Science, Sungkyunkwan University, Suwon, 440-746, Republic of Korea

ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form
19 November 2015
Accepted 21 November 2015
Available online 24 November 2015

Keywords:
Nitride materials
Nanostructured materials
Nanofabrications
Scanning electron microscopy
Optical spectroscopy
Luminescence

ABSTRACT

The light emission mechanism of green InGaN-based light-emitting diodes (LEDs) coated with ZnO nanorods (ZnO-nanorods/InGaN LEDs) was investigated by confocal scanning electroluminescence (EL) spectroscopy (CSEM). The ZnO nanorods were grown by a hydrothermal method on the surface of fully fabricated InGaN LEDs. The vertical alignment and high crystallinity of the ZnO nanorods were confirmed by scanning electron microscopy, X-ray diffraction, photoluminescence spectroscopy, micro-Raman spectroscopy, and high-resolution transmission electron microscopy. Measurement of the light output as a function of the injection current, far-field radiation pattern, and current versus voltage curves revealed that the light output power of the green InGaN LEDs with ZnO nanorods was enhanced by approximately 60% compared to that of conventional green InGaN LEDs without ZnO nanorods. However, the electrical properties of the ZnO-nanorods-coated device were not appreciably affected by the nanorods. To analyse the light emission mechanism of the ZnO-nanorods/InGaN LEDs, CSEM was used to observe the EL intensity distributions at different focal planes.

1. Introduction

GaN-based light-emitting diodes (LEDs) have been extensively studied for solid-state lighting applications because of transferable, flexible characteristics of the LEDs with significantly lower energy consumption than conventional incandescent light bulbs [1–4]. In particular, InGaN active layers in LED are providing enormous practical benefits for producing full-colour displays because of the tunability of the energy gap over the entire visible spectrum [5–8]. Nevertheless, their low light extraction efficiency (LEE), which is attributed mainly to the low probability of photons escaping from the LED structure, must be improved to advance the development of high-performance InGaN-based LEDs [9–12]. The low LEE is caused by the large difference (approximately 1.5) between the refractive indices of the LED surface and air, which typically results in decreased photon transmission [13–15]. Furthermore, the external quantum efficiency (EQE) of InGaN-based LEDs drops dramatically in the green region of the visible spectrum, which is the easiest colour for the human eye to sense. This low EQE of green LEDs, irrespective of the material system, is called the 'green gap' [16–19]. To increase the light emission efficiency of green LEDs, several research groups have developed various techniques for crystal growth and for modifying the surface of LEDs [20–22]. Zhao et al. [23] proposed that the internal quantum efficiency of green InGaN LEDs could be increased by using the optimum quantum-well structure. Kang et al. [24] reported that the LEE of green InGaN LEDs increased upon application of an anti-reflection layer composed of ZnO nanorod arrays on top of the LEDs, which was deposited by radio frequency magnetron sputtering. However, these methods are consuming high cost.

Recently, ZnO micro-/nanostructures grown by a hydrothermal method have been used to enhance the light output power of blue InGaN LEDs without altering their electrical properties, because this method is a self-assembly process performed at low temperatures (around 150 °C) [25–32]. Since industrial processes typically require simple, rapid, and low-cost techniques, the hydrothermal growth of ZnO micro-/nanostructures is one of the most attractive techniques for enhancing industrially produced LEDs. Nevertheless, hydrothermal growth of ZnO nanorods onto green InGaN LEDs for improving the LEE has not yet been reported. Moreover, evidence such as direct observation of the light propagation through ZnO nanorods on the InGaN LEDs remains unsatisfactory.

* Corresponding author. Department of Energy Science, Sungkyunkwan University, Suwon, 440-746, Republic of Korea.
E-mail address: mjeong@skku.edu (M.S. Jeong).

http://dx.doi.org/10.1016/j.jallcom.2015.11.151
0925-8388/

In this study, the enhanced light output power of green InGaN LEDs coated with a layer of ZnO nanorods (ZnO-nanorods/InGaN LEDs), which were grown by a hydrothermal method, was investigated. Confocal scanning electroluminescence (EL) microscopy (CSEM) was used to directly observe the intensity of the light propagating through the ZnO nanorods. The optical and structural properties of the ZnO nanorods were examined by photoluminescence (PL) spectroscopy, Raman scattering, and high-resolution transmission electron microscopy (HR-TEM) measurements. The performance of the green LEDs was verified through measurement of their EL spectrum and driving current as a function of the operating voltage.

2. Experimental methods

2.1. ZnO nanorods

To prepare the reaction solution, zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$), was dissolved in deionised water to obtain a 0.05 M solution at room temperature. To form an alkaline reaction environment (pH 9) in the solution, NH_4OH was added until the desired pH was achieved. All hydrothermal processes were performed for 60 min at 150 °C in an autoclave. The pressure and heating rate in the reactor were 4 atm and 3 °C s^{-1}, respectively.

2.2. Measurements

The morphology of the ZnO nanorods on the green InGaN LED was observed by field-emission scanning electron microscopy (FE-SEM, S-4700, Hitachi), and the crystal direction of the ZnO nanorods was determined by X-ray diffraction (XRD). The optical properties of the ZnO nanorods were measured by PL spectroscopy, which was performed using a macro-PL spectrometer equipped with a He–Cd laser ($\lambda = 325$ nm). Raman scattering measurements were performed using a micro-Raman system equipped with a He–Ne laser ($\lambda = 633$ nm) to verify the crystal structure of the ZnO nanorods. For the spectroscopic analysis, a 30-cm monochromator (SP2300, Princeton Instruments) was used to disperse the light collected from the samples and a thermoelectrically cooled charge-coupled device (PIXIS100, Princeton Instruments) was used as a photodetector. The high crystallinity of the ZnO nanorods was verified from HR-TEM images and selected-area electron diffraction (SAED) patterns. The device performance was measured using a conventional probe station system equipped with SourceMeter 2400 (Keithley). The CSEM system consisted of an optical confocal microscope equipped with a lead zirconate titanate (PZT) nanopositioner, an optical fibre, a power supply, and an external signal modulator.

3. Results and discussion

3.1. Structure of green InGaN LEDs

The epitaxial structure of the green InGaN LEDs was fabricated by metal-organic chemical vapour deposition on *c*-plane sapphire substrates. Fully fabricated LED chips were obtained by conventional LED fabrication processes, with the LED structure having the schematic shown in Fig. 1(a). The green InGaN LEDs consist of an undoped GaN layer as the buffer layer, an n-type GaN layer as the electron injection layer, five pairs of InGaN/GaN multiple quantum wells (MQWs) as the active layer, a p-type GaN layer as the hole injection layer, an indium tin oxide (ITO) transparent conducting layer as the current spreading layer, and a Cr/Au layer as the electrodes for both the n- and the p-type GaN layers. The ZnO nanorods were then grown on the ITO layer by a hydrothermal method at 150 °C for 1 h. The schematic of the final structure of the ZnO-nanorods/InGaN LEDs is shown in Fig. 1(b), and the layers of the final device are depicted in the magnified schematic in Fig. 1(c).

3.2. Alignment of ZnO nanorods

The plane- and side-view field-emission scanning electron microscopy (FE-SEM) images of the ZnO nanorods grown on the green InGaN LED are shown in Fig. 1(d) and (e), respectively. These images show that all the ZnO nanorods are perpendicular to the LED surface. The ZnO nanorods have an average diameter of 60 nm, length of 500 nm, and periodicity of approximately 80 nm. To determine the crystal direction of the ZnO nanorods, the XRD pattern of ZnO nanorods grown on a *c*-plane sapphire substrate was measured. It should be noted that the ZnO nanorods were grown on both the sapphire substrate and the LED simultaneously in the same reactor. As shown in Fig. 1(f), the peaks in the XRD pattern at 34.2° and 72.5° correspond to the (002) and (004) planes, respectively, of the ZnO nanorods [33]. The weak peak at 41.3° originates from the *c*-plane sapphire substrate [34]. Therefore, the only peaks present are those for a *c*-plane-oriented ZnO crystal, which implies that the ZnO nanorods used in this study are regularly grown along the *c*-axis.

3.3. Optical and structural properties of ZnO nanorods

The optical and structural properties of the hydrothermally grown ZnO nanorods were measured by macro-PL spectroscopy, micro-Raman scattering, and transmission electron microscopy (TEM). Fig. 2(a) shows the room-temperature PL spectrum of the ZnO nanorods when excited with a He–Cd laser ($\lambda = 325$ nm). As can be seen from this figure, a strong and sharp near-band-edge (NBE) emission is present at around 382 nm, and a broad, weak, yellow band exists from 500 to 700 nm. This broad, yellow luminescence centred at 600 nm is associated with two specific defects: oxygen vacancies and the recombination of photogenerated holes with singly ionised charge states [35,36]. The stronger NBE peak than the defect-related yellow band in the PL spectrum indicates that the ZnO nanorods have high crystallinity. The micro-Raman spectrum was measured in a backscattering geometry with a He–Ne laser ($\lambda = 633$ nm) used as the excitation source. Fig. 2(b) shows the Raman spectrum of the ZnO nanorods grown on the *c*-plane sapphire substrate. The spectral resolution for Raman spectroscopy was ~0.5 cm^{-1}. The black arrows indicate the main Raman peaks of the sample. The peaks at 379, 418, 578, and 751 cm^{-1} are the Raman peaks related to the *c*-plane sapphire substrate. The peak at 439 cm^{-1} corresponds to the E_2^{high} optical phonon mode of the ZnO nanorods, which indicates that the nanorods have a hexagonal wurtzite structure [37]. Fig. 2(c) shows a low-resolution TEM image of an individual ZnO nanorod that was washed off the as-prepared product. A HR-TEM image and the corresponding SAED pattern are shown in the top-left and bottom-right insets, respectively. The spatial resolution for HR-TEM is approximately 0.1 nm. The HR-TEM image shows a lattice spacing of approximately 0.52 nm in the direction of the longitudinal axis, which corresponds to the d-spacing of ZnO (001) crystal planes [38]. The SAED pattern also indicates the *c*-plane crystal direction of the individual ZnO nanorod. These results confirm that the ZnO nanorod has a highly crystalline, single-domain hexagonal wurtzite structure.

3.4. Device performance

The performance of the ZnO-nanorods/InGaN LED was investigated through measurement of the current–voltage (I–V) and light output versus injection current (L-I) curves, as well as the far-field