Fabrication and Characterization of Light Emitting Diode Based on n-ZnO Nanorods Grown Via a Low-Temperature

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Abstract. In this work, we report the fabrication of a near-ultraviolet (UV) light emitting (LED) device based on the growth of n-ZnO nanorod (NRs) arrays on the p-GaN layer/sapphire substrate heterostructure using the low-cost hydrothermal technique. Morphological, structural and optical properties of the as-fabricated sample are described. The room temperature current-voltage (I–V) measurements of the fabricated LED device confirmed a rectifying diode behaviour. The device presents near UV color under reverse bias. The luminescence properties were investigated from both sides of the fabricated LED device at room temperature by electroluminescence (EL). EL spectrum of color emitting LED composed of intense peaks centered at 367 nm, 379 nm and a broad band around green emission. EL emission for the device has seen with the naked eye under normal light.

1. Introduction

In recent years, ZnO nanostructures have received a considerable interest because of their prominent and unique properties which can be exploited for a huge range of nanotechnology applications such as UV detectors, chemical sensors, solar cells [1], biosensors [2], pH sensors, gas sensors [3] and UV light emitting devices (LEDs) [4]. ZnO is a semiconductor with the structure of hexagonal wurtzite (lattice constants of a= b= 3.25 Å and c = 5.2062 Å). It has a wide direct band gap energy (3.37 eV). ZnO is promising material for large potential applications, gas sensors, transparent conducting layers, light-emitting diodes (LEDs), ultraviolet (UV) lasers and UV detectors[5-7].

Both GaN and ZnO materials have similar in some of their properties such as low lattice constant misfit (~1.9%), thermal expansion and large band gap (~3.4 eV). Therefore, the p-GaN is a promising semiconductor for the growth of n-type ZnO nanorods to fabricate n-ZnO/p-GaN heterostructure light emitting diodes, photodetectors and solar cells due to near lattice matching.

To date, myriads of synthesis technique for the deposition of ZnO nanorods (ZnO NRs)-arrays have been developed. Among these techniques, chemical bath deposition (CBD) or hydrothermal deposition has attracted the most attention because it is an inexpensive and facile method. For instance, Vayssieres et al. (2001) have designed a low-cost process for the fabrication of highly oriented ZnO nanorods-arrays directly onto different type of substrates.

In this work, we exhibit the synthesis of vertically n-ZnO nanorods on the p-GaN substrate and fabricate UV LED device based on this structure by a simple hydrothermal system as low-cost method.
the device was characterized and measured its electrical properties by FESEM, EDX, current-voltage characteristics and EL measurement.

2. Experimental
In this study, all chemicals were used without additional purification. The aqueous Zn (NO3)2-HMTA chemistry is one of the most popular chemical bath deposition chemistries for the synthesis of ZnO nanorods on a substrate. The synthesis method has been reported in our earlier work [8], however, in brief, it can describe the experimental part in this work through three stages.

In the first stage, p-type GaN thin film (thickness: ~5µm) deposited on a sapphire substrate (thickness: 400µm), was purchased commercially and served as a substrate. In the cleaning process, Mg-doped p-GaN substrate was put into ethanol solution followed by the immersion in a diluted hydrofluoric acid solution. The substrate was then dried with nitrogen gas. Next, by using RF sputtering system, 150 nm thick ZnO seed/layer was deposited onto the Si substrate. Subsequently, to obtain ZnO seeds for CBD growth, the seeded silicon was put into the quartz tube of the lab furnace for the heat treatment in air at a temperature of 400 °C for 0.5 hours.

In the second stage, the sample was put into a screw-capped bottle (Schott bottle) containing an equimolar (0.08 M) aqueous solution of Zn (NO3)2·6H2O and hexamethylamine (HMT) as a precursor solution. To obtain the correct precursor concentrations, these two materials were separately dissolved in deionized (DI) water at temperature of 750 °C.

![Schematic figure of the hydrothermal method apparatus.](image-url)
In the third stage, the two solutions were then mixed in a bottle. Next, the bottle which contained the precursor solution as well as the sample was placed on a hot plate for 3 hours at a temperature of 90 °C (See Figure 1). Finally, the sample was rinsed initially with hot DI water and followed by the hot ethanol in order to remove the remaining salt. The substrates were then dried with nitrogen gas.

The morphologies of the ZnO nanorods were characterized using FESEM (FEI-NOVA NANOSEM 450) equipped with an energy-dispersive X-ray spectroscopy (EDX, Oxford instrument Analytical Ltd.). The current-voltage (I-V) measurement was investigated using Keithley 4200-SCS semiconductor characterization system. The electroluminescence spectrum of the n-ZnO NRs/p-GaN layer LED device was obtained by using Jaz Spectrometer Module (Ocean Optics).

3. Results and discussion

3.1. FESEM and EDX characterizations

Figure 2 shows the FESEM top images and cross section of ZnO NRs grown onto on p-GaN/sapphire substrate. The synthesized ZnO NRs for the sample are well crystallized with a hexagonal-like shape and regular vertical alliance with the diameter changing from 50 nm to 120 nm and length around 1650 nm. Furthermore, the ZnO nanorods have high-growth distribution density on the substrate.

Figure 2. FESEM top images and cross section of ZnO NRs synthesized on p-GaN/sapphire substrate.

Figure 3. displays the energy-dispersive X-ray spectroscopy spectrum of the as-deposited ZnO nanorods for the sample. Based on this figure, only Zn, O, Ga, N, and Al elements exist in the sample. This result corroborates the high purity of ZnO nanorods were grown on GaN/sapphire substrate.
3.2. Current–voltage characteristics

Figure 4 exhibits the results of current-voltage (I-V) characteristics for the n-ZnO NRs/p-GaN heterojunction LED device between the ITO contact on the n-ZnO NRs and the ITO/Ni contact on the p-GaN. The inset is the schematic diagram fabricated LED device. The device was fabricated as follows: prior to the growth of ZnO NRs on the p-GaN substrate, an ohmic contact ITO/Ni on p-GaN was made by RF sputtering. After the synthesized ZnO NRs on the p-GaN/sapphire substrate, the ohmic contact resistance was then reduced by putting the sample into the quartz tube of the lab furnace for heat treatment in the N₂ environment for 4 min at a temperature of 400 °C. Then, Polyvinyl alcohol (PVA) was used as an electrical isolation material to block a short circuit between the top ITO contacts with GaN material. From the figure 4, it can be noticed that the value of 4Eg/q (Eg ∼ 3.4 eV is the band-gap energy of ZnO or GaN) is larger than -6.5 V which is the approximate value of the reverse breakdown occurs for the device. Accordingly, one can conclude that the breakdown mechanism for the device is caused by the tunneling effect [9]. In addition, The I-V characteristics show good rectifying behaviour for the n-ZnO NRs/p-GaN heterojunction device.
3.3. Electroluminescence Characteristics

In this study, the EL emissions were measured from both sides of the device (ZnO side and transparent sapphire side). Figures 5 shows room-temperature EL spectra of the fabricated device measured from the ZnO NRs side (frontside) of the device when was supplied reverse current (voltage) of 8 mA (-14 V) and 16 mA (-22 V). It can be seen from Figure 5 that the LED device emission a UV light from the frontside which appear as the main peak is centered at ~389 nm. The right inset shows real optical photos of the LED in the ambient lighting at the current injection of - 22 V.

![Figure 5](image1.png)

**Figure 5.** EL measurement spectrum emission from frontside of the n-ZnO NRs /p-GaN LED with different current injections at the reverse breakdown bias. Top right inset shows real optical photos of the LED in the ambient lighting at the current injection of - 22 V.

While Figures 6 shows room-temperature EL spectra of the fabricated device measured from the transparent sapphire side (backside) of the device when was supplied reverse current (voltage) of 8 mA (-14 V) and 16 mA (-22 V). One can be observed from Figure 6 that the light emission color from the backside is made by composed of two peaks, the main peak at ~367 nm and with a satellite peak at ~379 nm, it is expected that the source of these two peaks are from the NBE irradiative recombination in p-GaN and n-ZnO, respectively [10]. The right inset displays the real optical photos of the LED in the ambient lighting at the current injection of - 22 V. Finally, One can be observed from both Figures 5 and 6, when the applied voltage was increased under the reverse voltage the EL intensity emissions from both sides are enhanced remarkably as well.
Figure 6. EL measurement spectrum emission from backside of the n-ZnO NRs/p-GaN LED with different current injections at the reverse breakdown bias. Top right inset shows real optical photos of the LED in the ambient lighting at the current injection of -22 V.

4. Conclusion

The low-cost hydrothermal process has been successfully utilized to grow vertically ultralong, well-aligned and hexagonal-shaped n-ZnO NRs on the p-GaN/sapphire substrate, and to be exploited for the fabrication of the n-ZnO NRs /p-GaN LED device. The results were confirmed by FESEM, EDX, I-V, and EL measurements. FESEM shows how vertically ZnO NRs were grown on the GaN surface. I-V characterizations confirm that the breakdown mechanism for the device is caused by the tunneling effect. The EL emissions were measured from both sides of the fabricated LED device.

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