Fabrication of a High-Brightness Blue-Light-Emitting Diode Using a ZnO-Nanowire Array Grown on p-GaN Thin Film

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Light-emitting-diode (LED) technology was originally developed from the high-efficiency electroluminescence (EL) of semiconductor devices in early 1962.[1] The high brightness, high efficiency and long durability of LEDs renders them ideal for displays and solid-state lighting.[2] Among the basic colors, LEDs covering green to violet light are still under intensive development due to the low efficiency of the available devices. Weak blue-LEDs fabricated from semiconducting SiC have been produced, but they are orders of magnitude less efficient than their red and yellow counterparts.[3] In recent years, with the development of metal organic chemical vapor deposition (MOCVD), gallium nitride (GaN) has become the most important building block for LEDs operating in the green to ultraviolet light range.[4–7]

UV–blue LEDs using single GaN nanowires (NWs) have also been fabricated, and nanoLEDs are an active field of research.[5,8] However, GaN NWs and especially aligned NW arrays are difficult to grow. Attempts have been made to find substitutes to replace GaN NWs.[9–14] To overcome the limited availability of GaN NWs and take advantage of their ideal blue-light emission, development has begun of so-called hybrid p–n heterojunction LEDs, which are composed of heterojunctions between oxide-semiconductor NWs and GaN p-type thin layers.[12,13,22] The p-type organic heterostructure has also been studied.[20,21] Among all of the known oxide semiconductors, ZnO NWs are the top choice for blue emission not only because of their superior properties, with a wide band-gap (3.37 eV) and a large exciton-binding energy (60 meV), but also due to their easy growth via chemical and physical vapor-phase approaches.[15,16] It is known that ZnO NWs can be grown following a designed pattern into aligned arrays on almost any substrate in any shape.[17]

In this paper, we report the fabrication of high-brightness n-ZnO NWs/p-GaN film hybrid heterojunction LED devices by directly growing n-type ZnO nanowire arrays on p-GaN wafers. A UV–blue electroluminescence (EL) emission was observed from the NWs–film heterojunction diodes. The emission spectrum shifted towards short wavelengths, with an increase in forward bias applied to the device, with p-GaN as positive. In addition, the heterojunction LED device exhibited a high sensitivity in responding to UV irradiation.

The hybrid (n-ZnO NWs)/(p-GaN film) LED device (Fig. 1a) was first fabricated by growing a ZnO nanowire array on a (0001) GaN film, with sapphire as the substrate and using the physical vapor-deposition process.[16,18] The NWs grown had a uniaxial orientation of (h001) with an epitaxial orientation with respect to the GaN substrate, for (n-ZnO NWs)/(p-GaN film) hybrid heterojunctions. The current–voltage (I–V) characteristic of the (n-ZnO NWs)/(p-GaN film) LED device is shown in Figure 1b. The I–V curve clearly shows a nonlinear increase of current under the forward bias, which indicates reasonable p–n junction characteristics and the possibility of light emission. The turn-on voltage of the hybrid heterojunction of ZnO/GaN (NWs/film) is around 3 V, as shown in Figure 1c.

![Figure 1.](https://placecase.com/)

Figure 1. a) Schematic illustration of the (n-ZnO NWs)/(p-GaN film) hybrid heterojunction LED device. b) I–V curve of the ZnO/GaN heterojunction diodes from –5 to 40 V; the current reached saturation beyond 37 V. c) I–V curve of the ZnO/GaN heterojunction diodes from –5 to 12 V. The turn-on voltage is around 3 V.
Figure 2 shows scanning electron microscopy (SEM) images of the ZnO nanowires and the ZnO/GaN hybrid structure. ZnO NWs are about 100–150 nm in diameter with a sharp tip, lengths of around 5 μm, and form fairly uniform arrays on the substrate. From the cross-sectional image of the as-grown sample, each NW grew up independently from the GaN film, and there was no ZnO film at the bottom of the NW array. Therefore, the light emission is from the junction between the NW and the GaN film.[11]

A plot of electroluminescence (EL) intensity versus forward bias by fixing the emission wavelength at 400 nm is shown in Figure 3a. The inset is a typical lighting image of the (n-ZnO NWs)/(p-GaN film) LED device of size 5 mm/2 × 3 mm recorded using a commercial digital camera Nikon D70 (70 mm lens, aperture f/5, exposure time 3 min). The LED device was placed on a stage inside the EL measurement instrument. The blue–light emission is strong enough to be clearly seen by the naked eye. The visible scales in the image were illuminated by the emission light while the background was completely dark. The emission light became visible to the naked eye when the bias voltage exceeded ~10 V, and the intensity increased rapidly when the forward bias was larger than the threshold. The response of the EL intensity to a pulse of +30 V is shown in Figure 3b, displaying good reproducibility and a rapid response.

The EL spectrum of the (n-ZnO NWs)/(p-GaN film) LED device was measured under various forward bias voltages (10, 15, 20, 25, 30, 35 V). As shown in Figure 4a, the EL spectrum showed broad emission peaks from UV to blue. Herein, light emission from the LED device was observed only under applied forward bias, which agrees with most LED reports.[20,21,23,24] Of course, there are still a few reports that argue using reverse-bias voltages to stimulate EL emission.[22] UV emissions around 370 nm were observed as well as strong peaks centered at 400–440 nm wavelength, which are quite broad and extend beyond 300 nm. With the increase of forward bias from 10 to 35 V, the emission peak was significantly enhanced. However, below 10 V the emission intensity was too weak to be detected. More importantly, the main emission peak shifted from 440 to 400 nm when the forward bias was increased.

We now use the band structure model to understand the shift in emission light with the increase of bias voltage, as shown in the insets in Figure 4b and c. Under the driving force of an applied electric potential, the holes in the valence band of p-GaN move towards the ZnO NWs, and the electrons in the conduction band of the ZnO NWs move towards the GaN. At the interface, the recombination of an electron and hole produces a photon with relatively smaller energy. This is the case when the applied bias is small (Fig. 4b). The threshold value at forward bias, in our case, is around 10 V, which corresponds to a 440 nm (2.8 eV) emission (Fig. 4a), the energy gap between the conduction band of ZnO and valence band of GaN at the interface. However, the potential profile at the interface depends on the magnitude of the applied voltage. If the externally applied voltage is larger than a threshold.
value at forward bias, the carriers may possess higher energy, and the barrier at the interface will become thinner. Thus, the electrons in the conduction band of ZnO and holes in the valence band of GaN have a higher possibility of being driven directly across the interface without recombination (Fig. 4c). These electrons will lead to the band-edge emission of GaN (387 nm), and the holes will lead to the band-edge emission of ZnO (368 nm). However, the recombination at the interface still contributes to light emission. Both band-edge emissions and interface recombination result in the broadening of the emission peak as well as the blue shift. The relative intensity of the ZnO emission increases with the increase of applied voltage, leading to a continuous shift of the emission peak towards higher energies.

It is known that UV excitation in ZnO can generate excess charge carriers. It is interesting to examine the influence of carrier density on the EL behavior. The response of the EL from the (n-ZnO NWs)/(p-GaN film) heterojunction diode to UV-light illumination was studied. Since the decay of UV-stimulated conductance in ZnO lasts for up to several hours, we can simply measure the EL output of the device after turning off the UV light, to avoid the interference of UV light with our measurement. We first illuminated the heterojunction device for 10 min using an UV lamp of wavelength of 365 nm. Figure 5a shows a series of EL emission spectra from the ZnO/GaN heterojunction diodes as a function of time after turning off the UV illumination. The overall EL intensity was enhanced as soon as the UV was turned off, and reached its maximum at ~30 min. The intensity then dropped. From our previous study,[19] UV illumination can not only increase the carried density but also reduce the height of the Schottky barrier at the interface. The overall EL intensity increased within 30 min of UV illumination being switched off, which was likely due to the high concentration of residual charge carriers created by UV and the charge-trapping effect from the vacancy states in ZnO. After the UV had been off for 30–150 min, the residual carriers were largely recombined, resulting in a drop in the EL intensity. UV light can effectively create electron–hole pairs, which is most likely the reason why the intrinsic band-gap emission peak at 370 nm was largely reduced when UV illumination was on, and quickly recovered after it was switched off. Figure 5b shows the EL emission intensities at wavelengths of 370 and 400 nm as a function of time after UV illumination was turned off. It seems that the UV illumination affected the emission at 370 nm more strongly than that at 400 nm, indicating that UV illumination strongly affects the band-edge emission.

In summary, we have demonstrated high-brightness UV–blue EL from n-ZnO/p-GaN (NWs/film) hybrid heterojunction LED devices. A blue shift was observed in the EL with the increase of bias voltage, indicating the modification of external voltage to the band profile in the depletion region. This means that the emission color can be slightly tuned by bias voltage. The EL intensity was affected after UV illumination due to the residual charge carriers excited by UV and the change in p–n junction energy gap. The 370 nm UV emission was first enhanced and
then dropped after UV illumination, indicating its stronger dependence on density of charge carriers in ZnO. The 400 nm blue emission was less dependent on the UV excitation. This study demonstrates the possibility of using ZnO NWs–GaN film heterojunctions for blue-light emission.

1. Experimental Details

The ZnO-NW array was synthesized on p-type Mg-doped GaN films with a sapphire substrate using chemical vapor deposition. A gold catalyst layer 2 nm thick was deposited by sputtering onto the GaN film substrate. The ZnO nanowires were grown through a vapor–solid process using pure zinc powder (99.9%) as the source material. The GaN wafer was located downstream from the source in a single-zone tube furnace. Argon was used as carrier gas at a flow rate of 49 cm$^3$ min$^{-1}$ (STP) with 1 cm$^3$ min$^{-1}$ (STP) oxygen to support the reaction. The tube furnace was heated to 950 °C at 50 °C min$^{-1}$, and held at this temperature for 40 min under a pressure of 10 Torr. The tube was then cooled in air to room temperature under argon flow.

A NWs-film LED device was fabricated by the following procedure. A11 poly(methyl methacrylate) (PMMA) was spin-coated on the ZnO-NWs array with a rotation rate of 4 000 rpm for 2 min to get a smooth surface for the subsequent film deposition. Oxygen plasma etching was then applied to remove the PMMA coated on the surface of the exposed ZnO NWs, by flowing 30 cm$^3$ min$^{-1}$ (STP) oxygen in an 8 $\times$ 10$^{-3}$Torr vacuum with etching power 50 W for 2 h. After that, an indium-tin-oxide (ITO) film (300 nm) was deposited by radio-frequency (RF) magnetron sputtering in a vacuum of 5 $\times$ 10$^{-3}$ Torr. Finally, two copper wires were attached on the surface of the exposed GaN and ITO films using silver paste as electrodes.

The morphology of the as-grown ZnO-NWs array was characterized using LEO 1530 thermally-assisted field emission (TFE) scanning electron microscopy. Digital pictures were taken using a Nikon D70 camera. J–V measurements and forward bias applied to the LED device were carried out using a Semiconductor Characterization System (Keithley 4200). The EL of ZnO/GaN heterojunctions for blue-light emission.

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