Graphene/ZnO Nanowire/p-GaN Vertical Junction for a High-Performance Nanoscale Light Source

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1. INTRODUCTION

Increasing demands for ever-increasing speed and functionalities of the communication networks call for scaling down of devices. Nanoscale light sources are promising for photonic and electronic devices, such as semiconductor on-chip integration of photonics and electronics, ultrahigh-resolution biomedical diagnostics, and unprecedented-capacity information storage. 1 Semiconductor heterojunctions based on one-dimensional (1D) nanostructures and p-type substrates are an ideal choice for the high-performance nanoscale light source. 2,−4

ZnO has attracted considerable attention for ultraviolet (UV) light emitters because of its bandgap of 3.37 eV and exciton binding energy of 60 meV. 5−7 One-dimensional ZnO micro- and nanostructures with good crystallinity, smooth boundaries, and excellent waveguiding properties can be used as natural waveguides and resonant microcavities. 8 However, it is still a challenge to obtain high-quality p-type ZnO materials. Alternatively, high-quality p-GaN offers an excellent platform to construct the p–n junction with n-ZnO. 9−12

ZnO nanowires/p-GaN heterojunctions have sparked considerable interest for nanoscale solid-state light emitters. 13,14 In the previous work, by simply placing ZnO nanowires on p-GaN thin films with a Pt contact at one end of the nanowire, we obtain UV light. In this structure, electrons could be injected from the small section of the nanowire, and the current injection area is restricted by the diameter of the nanowire. 15 In the single-nanowire electrically driven laser based on the n-Cds nanowire/p-Si heterojunction, electrons can be injected into the CdS nanowire. 16 A vertical injection structure based on ZnO-microrod/p-GaN has been reported by Dai et al., who have realized the electrically pumped Whispering-Gallery-Mode lasing. 17 Among these structures, increasing the carrier injection efficiency is crucial.

Graphene has attracted great research interest recently because of its unique properties of high mobility (as high as 26,000 cm 2 V −1 s −1 at RT), 18 and conductivity (sheet resistance of 200 Ω per square), 19 low optical absorption rate of 2.3%, 20 high chemical stability, as well as high mechanical elasticity (elastic modulus of about 1 TPa). 21 In contrast to opaque metal electrodes and indium tin oxide electrodes, 22 graphene sheets, with extremely high optical transparency, good conductivity, and simple damage-free fabrication, are suitable for applications in the fields of nanoelectronics as transparent window materials and high-quality electrodes. 23−25

In this work, we report on a nanoscale light source based on the graphene/ZnO nanowires/p-GaN vertical junction. In this structure, we used a vertical junction and transparent flexible graphene electrodes, which can enfold the upper surface of the ZnO nanowire and increase the carrier injection area. Moreover, it is found that the ZnO nanowire-based light emitters exhibit stronger UV electroluminescence (EL) emission of 397 nm at one end of the ZnO nanowire. This work provides a route for developing a high-brightness UV nanoscale light source on the basis of ZnO nanowires.
2. RESULT AND DISCUSSION

Figure 1a shows a scanning electron microscopy (SEM) image of a typical ZnO nanowire grown by a chemical vapor deposition (CVD) method. A perfect hexagonal cross-section and smooth side facets are observed, which means that the ZnO nanowire is of high quality and can act as an optical waveguide. Figure 1b shows the optical image of the fabricated n-type ZnO nanowire/p-type GaN film heterojunction; (c) schematic of the basic structure of the graphene/ZnO nanowire/p-GaN vertical junction and the test circuit.

Figure 2. Optical images of the EL spot of the n-ZnO nanowire/p-GaN heterostructure device at different forward biases of (a) 0 V, (b) 30 V, (c) 50 V, (d) 100 V, (e) 150 V, and (f) 200 V. The area of the graphene/n-ZnO nanowire/p-GaN heterojunction, the terminal area of the ZnO nanowire, and the damage area of ZnO nanowire pressed with glass needle tip are pointed by yellow, red, and green arrows in (c), respectively.

As the devices are applied with proper forward bias, a very bright emitting light can be observed directly by naked eyes. Figure 2a–f shows optical images of the EL spot of the n-ZnO nanowire/p-GaN heterostructure device under different forward biases from 0 to 200 V. The good performance of the light source implies that the assembling procedure of a simple direct contact between ZnO nanowire and p-GaN film is effective to produce the interface of the ZnO nanowire and p-GaN for a high-quality p–n heterojunction. As the forward bias increases, more and more intense blue-violet emissions can be seen from the graphene/n-ZnO nanowire/p-GaN heterojunction area, which is also the carrier vertical injection area, as denoted by the yellow arrow in Figure 2c. A blue-violet emission can also be seen at the end of the ZnO nanowire, which implies the ZnO nanowire can serve as an optical waveguide and the end of the ZnO nanowire can serve as a nanoscale light source, as denoted by the red arrow. If the ZnO nanowire is damaged due to being pressed with a glass needle tip at certain point, a blue-violet emission can also be seen from this pressed point, as denoted by the green arrow.

Figure 3a shows the EL spectrum of the n-ZnO nanowire/p-GaN heterostructure device at room temperature obtained from the body of the nanowire enfolded by graphene at different forward biases. The EL spectrum shows a broad near-UV emission peak centered at ~400 nm with the forward bias from 20 to 100 V, and the emission band extends unsymmetrically to 470 nm. Through Gaussian deconvolution analysis, the broad emission is decomposed into three distinct emissions, as shown in Figure 3b, which correspond to three different optoelectronic processes. To further confirm the physical origin of the EL emission, measurement of the selected area of photoluminescence (PL) under an incident laser of 325 nm was carried out, as illustrated in Figure S1a in the Supporting Information, with the illumination area given in the inset. The energy barriers at the n-ZnO/p-GaN junction are formed. The three recombination processes considering the interfacial barriers are illustrated in the energy band diagram, as shown in Figure 3c. According to the analysis of the interfacial energy band renormalization and the emission spectrum, the barrier of 0.35 eV for electrons and 0.33 eV for holes are extracted. Therefore, the EL is from the n-ZnO, p-GaN, and the interfaces of the graphene/ZnO/GaN vertical junction.

A representative broad EL spectrum obtained from the body of the nanowire at 100 V is decomposed by multipeaks Gaussian fitting referring to the PL spectrum. Each spectrum includes three distinct subbands centered at ~393, 411,
438 nm, respectively, as shown in Figure 3b. Compared with the PL spectrum in Figure S1a, the UV emission band at 393 nm is from the near-band-edge (NBE) recombination in the ZnO nanowire, while the blue emission band at 438 nm is from recombination between the electrons in the conduction band and the deep Mg acceptor level in the p-GaN thin film. The emission band at 411 nm can be attributed to the radiative interface recombination of electrons from n-ZnO nanowires and holes from p-GaN films. As a result, the wide EL emission band is attributed to the superposition of a strong ZnO NBE recombination, a relatively weak interfacial radiation, and a very weak emission from the p-GaN film. As the applied voltage increases, the focus of the EL spectrum shifts to the UV direction. It is suggested that light emitting will concentrate more in the ZnO nanowire with the increasing applied biases, which is originated from the recombination of excitons in ZnO.

Figure 3d shows the relationship between the integrated intensity (L) of the EL peak and the applied biases (V). The results are fitted well by the power law of \( L \propto V^m \), where m
accounts for the influence of nonradiative defects on the light emission characteristics. The \( L-V \) curve in Figure 3d shows a superlinear dependency at a low voltage (<50 V) with \( m = 3.99 \) and a sublinear dependency at a high voltage (>50 V) with \( m = 0.56 \). In the previous work by Alivov and co-workers, the light-current \((L-I)\) characteristics of the n-ZnO/p-GaN film junction show a similar superlinear dependency for low currents (<10 mA) with \( m = 1.9 \), which changes to a sublinear \((m = 0.85)\) dependency for higher currents (>10 mA). Experimental investigation by Uji et al. on InGaAsP/InP LEDs has demonstrated that nonradiative recombination influenced strongly by the injected carrier density is responsible for the output saturation. The turning point in the \( L-V \) curve corresponds to the voltage value, where the nonradiative recombination is saturated and the energy conversion efficiency reaches a maximum. In the \( L-V \) curve fitted by the power law of \( L \propto V^m \), a superlinear phenomenon \((m = 3.99)\) at low voltages suggests that the increased rate of radiative recombination is much quicker than that of nonradiative recombination. The sublinear dependency \((m = 0.56)\) under high voltages is due to the saturation in nonradiative recombination and the decrease in electrical-to-optical conversion efficiency caused by Auger recombination or by Joule heating effects.

EL spectrum of the device at one end of the ZnO nanowire at different forward biases from 10 to 40 V is presented in Figure 4a. The profile of the EL spectrum does not change much with applied biases. The mechanism of EL can be interpreted by the same energy band diagram shown in Figure 3c, and a representative broad EL spectrum obtained from one end of the ZnO nanowire at 40 V is also decomposed with Gaussian functions referring to the PL spectrum. The superposition of a strong interface radiation \((408 \text{ nm})\), a relatively weak ZnO NBE recombination \((395 \text{ nm})\), and a very weak emission from p-GaN film \((432 \text{ nm})\) were obtained, as shown in Figure 4b.

As we have seen in the experiment result, the ZnO nanowire in the light emitters appears to support the guide modes that propagate along the c-axis though much of light leaked to the GaN substrate because of its larger refractive index. The possible field distribution of the guide modes and propagation loss are studied by FDTD simulation. The degenerated HE_{m0} modes splitting as the nanowire is on a substrate with refractive index larger than air. The two possibilities are labeled as HE_{nna} and HE_{num}. We find some lowest-order modes which have relatively less loss compared to the others though no stable-guided mode exists in the ZnO nanowire/p-GaN structure. The field distribution of four modes of them is shown in Figure 4c. The field amplitude versus propagation length are plotted, as shown in Figure 4d. TM_{01} mode has the smallest propagation loss of about 0.090 dB/μm or 3.6 dB for the 40 μm length. The propagation loss of HE_{11a}, HE_{11b}, and HE_{21b} are 0.22, 0.17, and 0.18 dB/μm, respectively. These four modes have relatively stable field distribution in tens of micrometers. Field energy of TE_{01} and HE_{21a} modes are quickly absorbed by the GaN substrate in several micrometers whose mode patterns will not be maintained in the nanowire. The other higher-order modes have more propagation loss.

3. CONCLUSIONS
In conclusion, the graphene/ZnO nanowire/p-GaN vertical junction light sources have been demonstrated. Each individual device acts as a high-performance nanoscale UV light source driven by a bias voltage. The investigation of PL and EL spectra indicates that the emission band has three distinct electron–hole recombination processes: a strong UV emission band centered at around 393 nm from the NBE emission in the ZnO nanowire, a relatively weak radiative recombination at the n-ZnO/p-GaN interface, and a very weak emission from the p-GaN film. This work reveals the physical mechanism and light output process of near-violet EL in the vertical graphene/ZnO nanowire/p-GaN thin film junction, and the demonstrated high-performance nanoscale light source should be useful for the future optoelectronic integration technology.

4. EXPERIMENTAL SECTION
4.1. Synthesis of ZnO Nanowires. ZnO nanowires were synthesized by a simple CVD method in a horizontal quartz tube furnace. Uniform mixture of high pure carbon powder and analytical pure ZnO powder (the atomic ratio of C and O is 1:1) were used as the zinc source. Mixed gases of Ar and O₂ with 100 and 3.0 sccm, respectively, served as a carrier gas and an oxygen source. The temperature was held at 1070 °C for 120 min and cooled step by step with an interval of 200 °C for 60 min.

4.2. Synthesis of p-Type GaN Film. Mg-doped p-GaN film was grown by metal–organic CVD. An intrinsic GaN layer \((2 \mu \text{m})\) was first grown on a \((0001)\) c-face sapphire substrate. Then, Mg-doped GaN layer \((1.75 \mu \text{m})\) was grown on the GaN buffer layer. The Mg-doped GaN layer was annealed at 750 °C in a nitrogen atmosphere for 20 min.

4.3. Device Fabrication. The Mg-doped p-GaN thin films were grown on c-plane sapphire substrates. First, Ni \((10 \text{ nm})\)/Au \((50 \text{ nm})\) electrodes were evaporated on p-GaN, followed by annealing at 500 °C for 5 min in an O₂ atmosphere to form an Ohmic contact. The 100 nm thick Al₂O₃ insulator layer was evaporated on the p-GaN surface through electron beam evaporation. Then, a series of 1–5 μm wide grooves exposing p-GaN were formed using the standard electron beam lithography technique. The CVD-grown high quality ZnO nanowire was transferred from the as-grown substrate using the glass fiber under an optical microscope and placed along the groove to form the n-ZnO nanowire/p-GaN heterostructure. The evaporated Au micro-stamp and the CVD-grown monolayer graphene micro-stamp were transferred using site-specific transfer-printing technique with poly(methyl methacrylate) as a carrier film. The graphene micro-stamp covered the ZnO nanowire as the top electrode, and covered part of the Au micro-stamp on the Al₂O₃ insulator layer to connect the external circuit. Thus, part of the graphene contacted directly with the ZnO nanowire, and another part of the graphene contacted with the Au electrode on Al₂O₃. Because the diameter of the ZnO nanowire was larger than the thickness of the Al₂O₃, the flexible graphene was supported by the ZnO nanowire and did not contact with the exposed p-GaN.

4.4. Characterization and Measurements. The PL spectra were measured by a microzone confocal spectroscope (Renshaw inVia microRaman system) using a He–Cd laser \((325 \text{ nm in wavelength})\). The EL measurements were also carried out by the same Renishaw optical system with a 20× optical microscope objective. The EL spectrum was collected vertically to the junction region of p-GaN and ZnO nanowires covered with transparent graphene electrodes, and the electric power was supplied by an Agilent B2912A Precision Source/Measure Unit. The current–voltage \((I-V)\) characteristics of...
the junction were measured by a Keithley-4200 semiconductor parameter analyzer. All measurements were carried out at room temperature. The forward biases with positive voltage were applied on the p-GaN.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03858.

PL spectrum of the GaN film, ZnO nanowire and the n-ZnO nanowire/p-GaN film heterojunction; Raman spectrum of graphene; I–V characteristics of the n-ZnO nanowire/p-GaN heterostructure device; and I–V characteristics of the p-GaN/Au electrode structure in the dark (PDF)

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**Notes**

The authors declare no competing financial interest.

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