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# High brightness light emitting diode based on single ZnO microwire

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ABSTRACT

The ZnO microwires were synthesized repetitively via chemical vapor deposition method. The high brightness light emitting diode based on the single ZnO microwire/p-GaN heterojunction was realized. A strong ultraviolet emission accompanied by a relatively weak defects-related emission was observed at room temperature photoluminescence spectra of single ZnO microwire. The *I–V* curve of the heterojunction diode showed obvious rectifying characteristics with a turn-on voltage of about 7 V. Under the forward injection current of 1.1 mA, the ultraviolet electroluminescence centered at 389 nm wavelength could be obtained based on the single ZnO microwire/p-GaN heterojunction diode.

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## 1. Introduction

As a direct wide band gap semiconductor (3.37 eV), zinc oxide (ZnO) possesses a large exciton binding energy of 60 meV, which is much larger than the thermal energy (26 meV), making the excitons thermally stable at room temperature. Its wide bandgap also endows ZnO a promising material with wide applications in the short-wavelength optoelectronic devices, such as light-emitting diodes (LEDs), photodetectors, UV laser diodes (LD), solar cell and so on [1–5]. The ZnO-based LEDs are thought to be a potential candidate for the next generation of blue/near-UV light sources. Several types of LEDs have been reported, such as p–n homojunctions [6,7], metal–insulator–semiconductor (MIS) junctions [8,9], p–n heterojunctions [2,10–13] and so on. However, the native defects, such as interstitial zinc and oxygen vacancies, make ZnO usually present n-type conductivity [14–16]. Furthermore, the low dopant solubility, the deep acceptor energy level, and the self-compensation of shallow acceptors resulting from native point defects in ZnO [17] also make it very difficult to obtain high-quality, repeatable and stable p-type ZnO, which greatly hinder the development of efficient ZnO-based optoelectronic devices. Most ZnO-based LEDs are p–n heterojunction structures, which are formed with different p-type materials such as GaN [2,18–22], Si [10], SiC [11], NiO [12], polymer [13] etc. Among these various p-type materials, GaN is the most promising candidate because of the same wurtzite crystal structure and low lattice mismatch between ZnO and GaN. Furthermore, the ZnO-based heterojunction LEDs have been realized by using ZnO thin film or its various nanostructures, including nanowires, nanorods and so on. The LEDs based on a single ZnO microwire are few reported, though it has many advantages compared with thin film and nanostructures, because it can avoid the presence of grain boundaries and reduce many surface defects. Furthermore, ZnO microstructures with good crystallinity and smooth boundaries can be easily fabricated using the cheap, simple and controllable method, and the single ZnO microwire can also act as natural microcavity for lasers according to our previous research [23], so it is feasible to obtain the low threshold ultraviolet lasing from single ZnO microwire.

In this Letter, LED based on the single ZnO microwire/p-GaN heterojunction was realized, in which the p-type GaN film acted as the holes injection layer, and the single ZnO microwire fabricated via chemical vapor deposition (CVD) was accompanied to fabricate the heterojuction. The *I–V* characteristics and the electroluminescence (EL) properties of the heterojuction diode were carefully studied.

## 2. Experimental details

ZnO microwires were fabricated by using CVD method in a horizontal tube furnace. A mixture of ZnO and graphite powders (1:1 in weight ratio) was loaded in an alumina boat serving as the source material. The growth details of ZnO microwires were described in our previous publication [23]. Previous the CVD process, the ZnO buffer layer (about 100 nm thick) was deposited on the Si substrate via radio frequency magnetron sputtering method at 400 °C, which serves as the nucleation template.

To construct the LED, the commercial GaN layer grown on sapphire substrate with holes concentration and mobility of $1 \times 10^{17}$ $cm^{-3}$ and 6.9 $cm^2V^{-1}S^{-1}$ was used to serve as the holes injection layer. The Ni and Au metals were partially deposited onto

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p-GaN layer by vacuum evaporation to serve as electrode. A photoresist layer was spin-coated on another part of p-GaN film. A channel with tens of microns in width was realized using lithography method. The ZnO microwires are so long (about 1 cm) that they are observed with naked eyes, and the single ZnO microwire was easily chosen and put into the channel. Finally, the ITO conductive glass was inverted and used as the top electrode in order to form ohmic contact between ZnO and ITO glass. The schematic diagram of the n-single ZnO microwire/p-GaN heterojunction device is shown in Figure 1.

The morphologies of as-grown samples were characterized by the filed emission scanning electron microscopy (FESEM). The photoluminescence (PL) measurement was carried out with a JY-630 micro-Raman spectrometer by using the 325 nm line of a He–Cd laser as the excitation source. The Current versus voltage ($I$–$V$) measurement of the LED was performed using Keithley 2611 system, and the EL measurement was carried out with a Hitachi F4500 spectrometer, in which a continuous-current power source was used to excite the structure. All the measurements were performed at the room temperature.

## 3. Results and discussions

The ZnO microwires are found in inner boat and on the surface of Si substrate. The typical FESEM image of as-grown individual ZnO microwire is shown in the inset of Figure 2. The average diameter of ZnO microwires is about several micron to tens micron with the length of about 1 cm. The room temperature PL spectra of the p-GaN thin film and a single ZnO microwire are shown in Figure 2. A strong emission peak centered at 388 nm is observed in ZnO microwire, corresponding to the near band edge emission of ZnO.

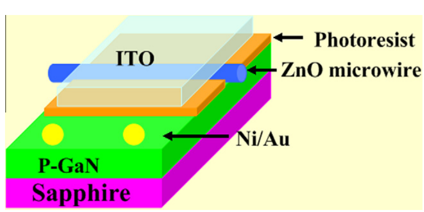


**Figure 1.** The schematic diagram of the n-single ZnO microwire/p-GaN heterojunction device.

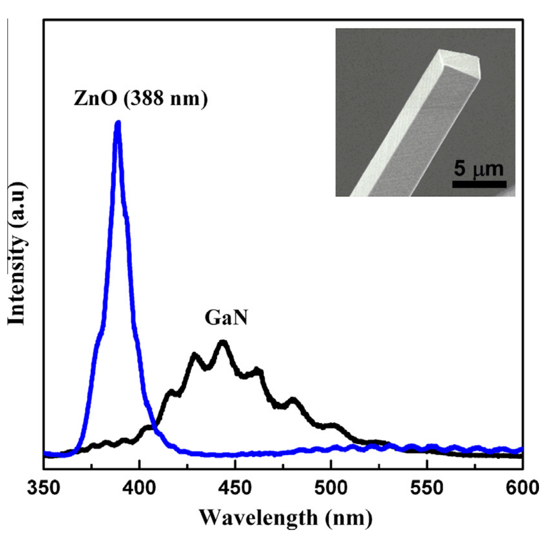


**Figure 2.** The PL spectra of the single ZnO microwire and P-GaN film at room temperature. The inset is the SEM of single ZnO microwire.

In addition, the defect-related emission is rather weak compared with the UV emission band, which includes several components: violet, green, and yellow. The green emission in ZnO is attributed to the recombination of electrons in singly occupied oxygen vacancies with photo-generated holes in the valence band [24]. The violet and yellow emissions are attributed to the radiative recombination of a delocalized electron close to the conduction band with a deeply trapped hole in the $V_{Zn}$ and $O_i$ centers [25], respectively. As for the broad PL spectrum centred at about 430 nm of GaN film, it can be attributed to the transition from conduction band electrons or shallow donors to the magnesium (Mg) acceptors [26]. Meanwhile, weak green emission related with the –/0 states of the $V_{Ga}O_N$ complex is observed. While the yellow luminescence resulting from the point defects like isolated Ga vacancies ($V_{Ga}$) [27] is absent with Mg doping, in agreement with its attribution to the $V_{Ga}$-containing defects. Moreover, the fringes observed in the spectrum are due to the thin film interference of the emitted light reflected by GaN/air and the sapphire/GaN interfaces [28,29].

Figure 3 shows the room temperature $I$–$V$ characteristics of the ZnO-based diode, from which the obvious nonlinear rectifying characteristics with turn-on voltage of about 7 V can be clearly observed. The Figure 3b and c present the $I$–$V$ curves of Ni/Au contacts to GaN film and the ITO contact with the ZnO microwire. The linear $I$–$V$ curve indicates that the ohmic contacts are obtained between these two kinds of contacts mentioned above. Based on these analyses, it can be concluded that the rectifying behavior of the LED originates from the single n-ZnO microwire/p-GaN film heterojunction. The $I$–$V$ characteristic of the heterojunction diode was further considered by plotting the current on log scale, which is shown in inset of Figure 3. The ideality of the diode can be determined from the diode equation,

$$I = I_s\left[\exp\left(\frac{eV}{nKT}\right) - 1\right] \quad (1)$$

$$n = \frac{e}{kT}\frac{dV}{d\ln I} \quad (2)$$

where $I_s$ is the saturation current, $k$ is the Boltzmann constant, $T$ is the absolute temperature, $e$ is the elementary electric charge, $V$ is the applied voltage, and $n$ is the ideality factor. According to Eq. (1) and Eq. (2), the value of the ideality factor of the heterojunction in our case is about 0.90 in left region (red line), and about 4.01 in right region (blue line). The deviation from the ideal case can be attributed to possible high contact resistance between GaN and ZnO.

By applying a forward bias to the heterojunction diode, the EL spectra are collected on the top of the device. Figure 4 shows the EL spectra of the heterojunction diode with different injection continuous currents (from 0.18 to 1.10 mA). The spectrum exhibits a broad peak centered at about 405 nm under lower driven current of 0.18 mA, and the intensity of the emission is rather weak. The intensities of emissions become stronger with the increasing of injection current. Meanwhile, a blue shift of peak position can also be observed when the injection forward current is increased. The UV emission peak centered at 391 nm appears with increasing the current to 1.1 mA, which is obvious asymmetric. The causes for this phenomenon are discussed according to the band diagram [19]. Under the driving force of an applied forward bias, the holes in the valence band of p-GaN can move towards the single ZnO microwire, meanwhile, the electrons in the conduction band of the ZnO microwire move towards the GaN. Under lower injection current (the emitting light is just observed), the emission peak centers at about 405 nm (as shown in Figure 4), which is contributed by the transitions from the conduction band edge of ZnO to the acceptor level of GaN at the interface, and the energy of the photon

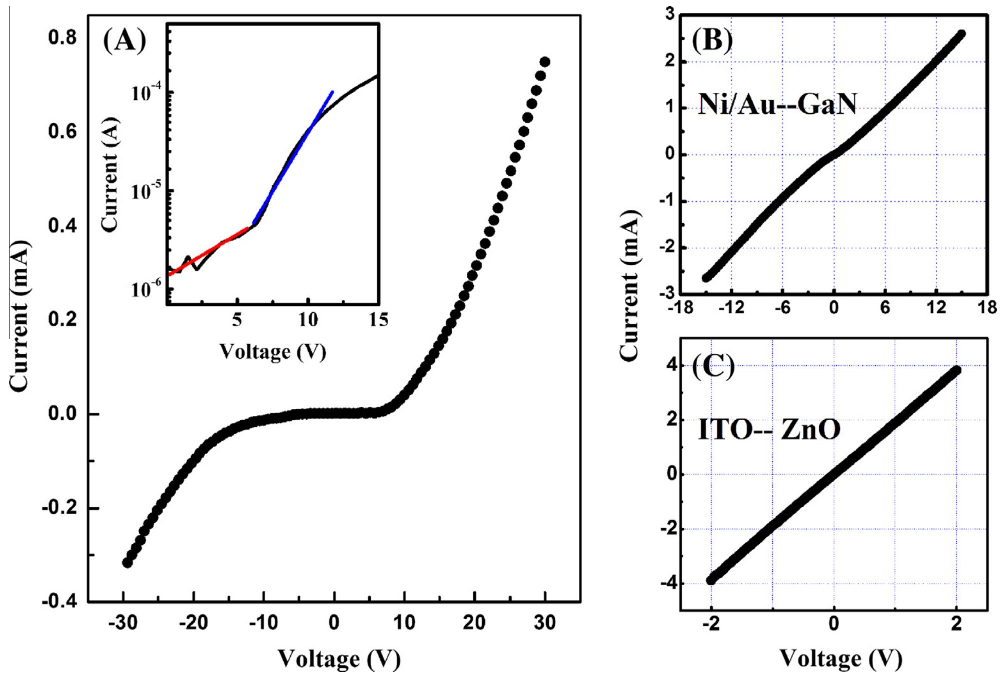


**Figure 3.** (a) The room temperature current–voltage characteristics of the single ZnO microwire/p-GaN film heterojuction based light emitting device. (b) The *I–V* curve of Ni/Au contacts to GaN film (c) The *I–V* curve of the ITO contact with the single ZnO microwire. The insets show the semi-log plot of current vs bias of Figure 3.

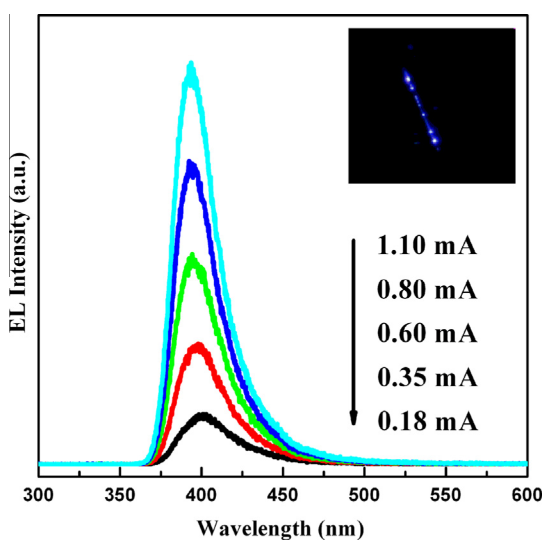


**Figure 4.** The room temperature EL spectra at different injected currents. The inset shows a typical emission photograph of the heterojunction diode taken at 0.6 mA.

is lower than the band gap of ZnO. When the applied forward injection current is much larger, the carriers have much more energy, and the potential barrier at the interface will become small. Therefore, it is entirely possible that the holes in the valence band of GaN are driven directly across the interface and reach the ZnO region. Meanwhile, the electrons in the conduction band of ZnO are driven directly across the interface, while few electrons and holes recombinate at the interface. The result shows that the recombination zone of EL emission is not only in ZnO microwire, but also at the interface between GaN and ZnO. For a small portion of holes that are injected into n-ZnO microwire from the p-GaN side, the EL located at 391 nm is realized, which is attributed to the near band edge emission from single ZnO microwire. A typical emission image of the heterojunction diode taken from the top of the device under an injection current of 0.6 mA is shown in the inset of Figure 4. It can be clearly observed that the emitting region presents line shape and uneven brightness. In another word, the whole single microwire can emit bright blue violet light, but the brightness of the microwire is uneven due to the uneven pressure exerted on the ITO glass.

To better understand the origin of EL emission peaks on such devices, the emission spectra are analyzed by Gauss fitting under the injection current of 1.10 mA, which could be fitted by three peaks (shown in the Figure 5), located at 389, 402, 425 nm, respectively. According to the reported results by other groups [30,31], the peak located at 389 nm is attributed to the near band edge from the single ZnO microwire, while the emission peak located at 402 nm is considered to originate from the transitions from the conduction band of ZnO to the acceptor level of GaN [32]. The peak located at the 425 nm wavelength could be attributed

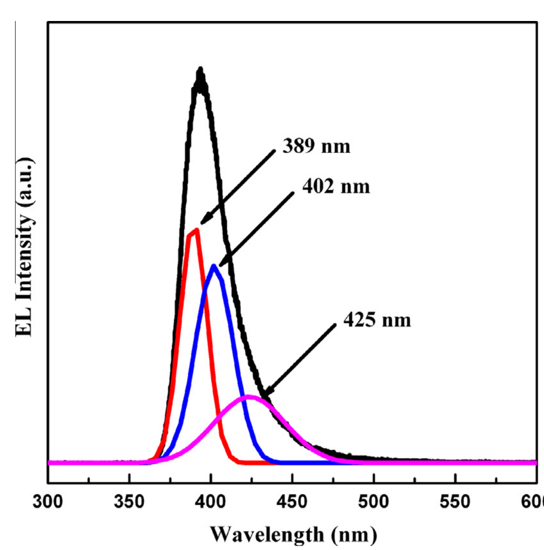


**Figure 5.** The EL emission peak (at 1.1 mA) fitted with three Gaussian peaks.

to the radiative recombination of electrons and holes in Mg doped GaN film, which is in accordance with the result of PL spectrum. As a result, the wide EL emission band under forward bias is ascribed to the superposition of a strong ZnO near band gap recombination, a relatively weak interfacial recombination, and a rather weak emission from p-GaN.

## 4. Summary

In conclusion, the ZnO microwires were fabricated repetitively via a simple CVD method. High brightness LED device is assemblied using the p-type GaN film acting as the holes injection layer. The ultraviolet EL centered at 389 nm wavelength could be realized under the forward injection current of 1.1 mA. This high brightness LED devices may have potential application prospects.

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