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#### Introduction

ZnO, a direct wide-band-gap semiconductor ( $\sim 3.37$  eV) with a large exciton binding energy of 60 meV at room temperature, has been regarded as one of the most promising candidates for optoelectronic devices, such as ultraviolet (UV) light-emitting diodes (LEDs), laser diodes (LDs) and photodetectors.<sup>1-9</sup> However, the lack of high quality, stable and reproducible p-type ZnO hinders ZnO-based homojunction devices.<sup>10</sup> In order to achieve electroluminescence (EL) from ZnO, an alternative successful method is to fabricate heterojunction devices by employing other available p-type materials (e.g., p-GaN,<sup>11,12</sup> p-Si,<sup>13</sup> p-NiO,<sup>14</sup> p-Cu<sub>2</sub>O<sup>15</sup> and p-type organics<sup>16</sup>). Among various p-type materials, GaN is one of the most promising candidates due to the same wurtzite crystal structure and the relatively small in-plane lattice mismatch (1.8%) with ZnO.<sup>17</sup> However, by analyzing the previous reported n-ZnO/p-GaN heterojunction LEDs, it can be found that most of the EL spectra for n-ZnO/p-GaN heterostructures are dominated by the defect-related visible emission (~420 nm) in p-GaN, and the UV emission in n-ZnO is always suppressed.<sup>7,11,12,18,23</sup> The reason for this trend is that the

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# Ultraviolet electroluminescence from a n-ZnO film/p-GaN heterojunction under both forward and reverse bias

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ZnO film was fabricated on p-GaN film using the molecular beam epitaxy technique to form heterojunction light emitting diodes (LEDs). The devices exhibited strong light emission under both forward and reverse bias. The origin of different luminescence peaks has been investigated by comparing electroluminescence (EL) and photoluminescence spectra. When a forward bias is applied to the device, intense ultraviolet emission at ~376 nm originating from ZnO rather than GaN can be observed, which is associated with the larger hole mobility of p-GaN than the electron mobility of n-ZnO. Under the reverse bias, the device shows broad emission at 520 nm originating from deep level-related recombination in ZnO, emission at 430 nm from GaN, 376 nm from ZnO and weak emission at 408 nm from the interface with a lower injection current of 10 mA. As the injection reverse current increases to 20 mA, the EL emission at 376 nm exhibits a dramatic increase in intensity without a peak shift. The emission mechanism of the heterojunction LED is discussed in terms of interface states and energy band theory. Our findings in this work provide an innovative path for the design and development of ZnO-based ultraviolet diodes.

mobility of electrons in n-ZnO is higher than that of holes in p-GaN and thus electrons in ZnO more easily drift into GaN. In order to achieve ZnO excitonic emission, an electron blocking layer (EBL), such as MgO,<sup>19</sup> AlN<sup>20</sup> or Al<sub>2</sub>O<sub>3</sub>,<sup>21</sup> is commonly selected to insert between p-GaN and n-ZnO to form a PIN-type heterostructure. However, the EBL not only can effectively block electron injection from ZnO into GaN due to its large conduction-band offset, but also can prevent hole injection from GaN into ZnO.20 Moreover, introducing an EBL into n-ZnO/p-GaN heterostructures could usually increase the turn-on voltage of the device and could also complicate the device structure.<sup>21</sup> These problems hinder the development and application of ZnO-based heterojunction LEDs. Recently, highly efficient UV emission is demonstrated by controlling the interface polarization of p-GaN/n-ZnO,<sup>22</sup> but this is a very demanding process for the preparation of devices. Therefore, an easy and effective method to realize UV emission from ZnO in n-ZnO/p-GaN heterojunction LEDs is urgently needed.

Just as mentioned above, the key reason for the suppression of UV emission in n-ZnO is its higher mobility of electrons than that of holes in p-GaN. Thus, if the mobility of electrons in n-ZnO is reduced to less than the mobility of holes in p-GaN, the holes in GaN should more easily drift into ZnO and thus UV emission can be observed on the ZnO side. Following the above guidance, n-ZnO with lower electron mobility and p-GaN with higher hole mobility have been fabricated by molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD) in this

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work, respectively, which are used to form n-ZnO film/p-GaN heterojunction LEDs. The EL characteristics of the devices have been investigated, and an intense UV emission from the exciton recombination in the ZnO layer can be clearly observed under both forward and reverse bias conditions. Although this unusual EL emission of light under both forward and reverse bias has also been observed in the previous reported ZnO/GaN heterojunctions, the devices always exhibit light emission in the visible region.<sup>23,24</sup>

#### Experimental

The p-GaN film with high hole mobility was grown on a *c*-plane sapphire substrate by MOCVD. Trimethylgallium and ammonia were used as Ga and N precursors, respectively. Dicyclopentadienyl magnesium (Cp<sub>2</sub>Mg) was used as the p-type dopant. Hydrogen  $(H_2)$  was used as the carrier gas during the growth processes. Prior to deposition, the sapphire substrate was thermally cleaned under H<sub>2</sub> for 10 min at 1100 °C and then the temperature was decreased to 550  $^{\circ}$ C and a ~30 nm thick GaN nucleating layer was deposited. Subsequently, the temperature was ramped up to 1050 °C and 3 µm-thick undoped GaN was deposited. The unintentionally doped GaN was followed by a 1.2 µmthick Mg-doped GaN layer grown at 950 °C which was activated at 850 °C for 60 s by a rapid annealing system under a N<sub>2</sub> atmosphere. The carrier concentration and the mobility of the obtained p-GaN were  $\sim 2.7 \times 10^{17}$  cm<sup>-3</sup> and  $\sim 20.1$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. Then the ZnO film was fabricated on p-GaN by MBE. 6N-purity zinc held in thermal Knudsen cells and 5N-purity O2 activated in a radio frequency plasma source were employed as precursors. According to our previous reports,<sup>25–27</sup> to fabricate the ZnO film with relatively lower electron mobility, the oxygen flux, the growth pressure and the substrate temperature were fixed at 0.7 sccm,  $3 \times 10^{-3}$  Pa and 500 °C, respectively. In order to estimate its electrical properties, ZnO film directly grown on *c*-face sapphire with the same conditions was used as the control sample. Hall measurement showed that the electron concentration of the ZnO film was  $\sim 3.1 \times 10^{18}$  cm<sup>-3</sup>, and its mobility was only 1.7 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Ti/Au and Ni/Au ohmic contact electrodes were deposited by vacuum thermal evaporation on n-ZnO and p-GaN, respectively, followed by annealing in an air atmosphere for 5 minutes.

The morphological features of the ZnO film were characterized with a Hitachi S4800 field-emission scanning electron microscope (SEM). A Bruker-D8 Discover X-ray diffractometer (XRD) with Cu-K $\alpha$  radiation ( $\lambda$  = 1.54 Å) was used to evaluate the crystalline properties of the layers. The surface roughness of the GaN film was estimated by atomic force microscopy (AFM; Bruker, MultiMode-8). The transmission spectra of n-ZnO and p-GaN films were characterized using a UV-3101PC scanning spectrophotometer. The photoluminescence (PL) spectra of the samples were recorded using a JY-630 micro-Raman spectrometer with the 325 nm line of a He-Cd laser as the excitation source. The electrical properties of the ZnO and GaN films were investigated by a Lakeshore 7707 Hall measurement system. The current-voltage (I-V) properties were recorded by using a semiconductor parameter analyzer. EL measurements of the devices were carried out using a Hitachi F4500 spectrometer, and a continuous-current power source was used to excite the structure.

#### Results and discussion

Owing to the same wurtzite structure and the small lattice mismatch between ZnO and GaN, it is expected to fabricate



Fig. 1 (a) SEM image of n-ZnO film on the p-GaN/c-Al<sub>2</sub>O<sub>3</sub> substrate, the inset shows the cross-sectional SEM image of ZnO on the p-GaN/c-Al<sub>2</sub>O<sub>3</sub>. (b) The XRD patterns of the ZnO film/GaN heterojunction. (c) AFM image of p-GaN film. (d) Transmission spectrum of ZnO film and p-GaN. (e) PL spectra of n-ZnO film and p-GaN at room temperature.

high quality ZnO film on GaN. The top-view SEM image of ZnO grown on GaN/c-Al<sub>2</sub>O<sub>3</sub> is shown in Fig. 1a, and typical hexagonal shape structures can be clearly observed on the surface of ZnO. The inset shows the cross-sectional SEM image of the sample, which can be used to estimate the thickness of each layer (ZnO: ~630 nm; p-GaN: ~1.2  $\mu$ m). In order to further investigate the crystal structure, we performed XRD measurements on the ZnO/GaN heterojunction as shown in Fig. 1b. It is clearly seen that both ZnO and GaN are hexagonal wurtzite structures and grow along the *c*-axis on *c*-face sapphire. Notablely, owing to the small lattice mismatch, the (0002) diffraction peaks of ZnO and GaN partially overlap each other at around 34.5°. Fig. 1c shows the AFM image of the p-GaN film, and the flat surface of the GaN film with a root-mean-square roughness of about 1.36 nm can be clearly observed. Fig. 1d shows the transmission spectra of the n-ZnO film and p-GaN film on the sapphire substrate. The average optical transmission in the spectral range from 400 nm to 700 nm is above 85% for both ZnO and GaN films with very sharp absorption edges at about 379 nm and 366 nm, respectively. The room temperature PL spectra of ZnO and GaN are shown in Fig. 1e. In Fig. 1e, narrow near-band-edge (NBE) UV emission located at 376 nm can be clearly observed for the ZnO film, which is attributed to radiative exciton recombination. In addition, a relatively weak visible emission band located at around 520 nm related to oxygen vacancies or zinc interstitials can be found,<sup>28</sup> suggesting the high crystal quality of the ZnO film. As for the GaN film, the PL spectrum has a broad blue emission peak at 436 nm, corresponding to the transitions from the conduction band or shallow donors to deep Mg acceptor levels in GaN.<sup>29</sup>

Fig. 2 shows the *I*–*V* curve of the n-ZnO film/p-GaN heterojunction LED, and a weak rectifying behavior can be obtained. The schematic diagram of the device is drawn in the lower right inset of Fig. 2 with a size of  $3 \times 4 \text{ mm}^2$ . The linear *I*–*V* curves for both Ni/Au on p-GaN and Ti/Au on n-ZnO indicate that good ohmic contacts have been obtained for both electrodes as



Fig. 2 The current–voltage (*I–V*) curves of the n-ZnO film/p-GaN heterojunction LED, the upper left inset shows the ohmic contacts of Ni/Au and Ti/Au, and the lower right inset shows the schematic of the ZnO film/ p-GaN heterojunction structure.

shown in the upper left inset of Fig. 2. The weak rectifying behavior and the large leakage current of the n-ZnO film/p-GaN heterojunction LED may be due to the tunneling process at the interface.

The room temperature EL spectra of the n-ZnO/p-GaN heterojunction are illustrated in Fig. 3. The EL signal is collected from the top of the device. Under forward bias (see Fig. 3a), a dominant UV emission peak located at  $\sim$  376 nm can be clearly observed. Additionally, the EL intensity is enhanced with increasing the injection current, but the shape and the position of the UV peaks are almost not changed, indicating a stable light-emitting property of the LED. It should be noticed that the EL peaks are asymmetric with a tail on the long wavelength side. As shown in Fig. 3b, the EL emission peak obtained under an injection current of 12 mA can be fitted by four Gaussian-shape peaks at  $\sim$  376 nm,  $\sim$  408 nm,  $\sim$  430 nm and  $\sim$  520 nm. By comparing the PL and EL spectra of the samples, it can be concluded that the emission peaks at 376 nm and 520 nm are attributed to the NBE emission and the deep-level emission in ZnO, respectively. As for the emission at 430 nm, it can be ascribed to the transitions in p-GaN associated with the Mg acceptor level. In addition, the



Fig. 3 (a) Room temperature electroluminescence (EL) spectra of the n-ZnO/p-GaN heterojunction under forward bias. (b) The Gaussian curve fitting of EL spectra measured under forward bias at 12 mA.



Fig. 4 (a) Room temperature electroluminescence (EL) spectra of the n-ZnO/p-GaN heterojunction under reverse bias. (b-f) The Gaussian curve fitting of EL spectra measured under reverse bias at 10 mA, 15 mA, 20 mA, 25 mA and 30 mA, respectively.

interfacial recombination of the electrons from n-ZnO and the holes from p-GaN should be responsible for the blue emission at 408 nm.<sup>30</sup> Obviously, the EL spectra of the n-ZnO/p-GaN LED under forward bias are dominated by ZnO NBE emission in the UV range. More interestingly, this heterojunction LED can also emit strong UV and visible light under reverse bias. Fig. 4a shows the room temperature EL under various injection reverse currents. When the injection current is lower than 15 mA, the EL spectra is dominated by the blue emission. With increasing the injection current to 30 mA, the intensity of UV emission increases dramatically without any change in peak position, making it dominate the EL spectra. In contrast, the blue and yellow emissions improve slightly, and the blue emission band shows an obvious blue-shift with increasing the injection current. In order to clarify the origin of EL emission and its change with injection current, the EL spectra of the ZnO film/p-GaN heterojunction measured under injection reverse currents of 10 mA, 15 mA, 20 mA, 25 mA and 30 mA are decomposed into Gaussian functions (see Fig. 4b-f). All the EL spectra can be well-fitted by four Gaussian peaks located at about 376 nm, 408 nm, 430 nm and 520 nm, and the origin of these peaks has been already discussed in the previous section. As we can see, the intensities of all four sub-bands increase with increasing the injection current. The intensity of ZnO NBE emission (376 nm) increases much faster than the other three components, and it thus plays a dominant role when the injection current is higher than 15 mA. As a result, the EL spectra rapidly narrow with the increase of the injection reverse current. In addition, the relative intensity change between the interface emission (408 nm) and p-GaN emission (420 nm) could be responsible for the blue-shift of the blue emission band with increasing the injection current as shown in Fig. 4a.

To the best of our knowledge, this is the first time that UV EL is emitted from n-ZnO film/p-GaN film heterojunction

under both forward and reverse bias conditions. To better understand the EL properties of the n-ZnO/p-GaN heterojunction, Fig. 5 shows an illustrative diagram of the carrier recombination process in this diode. For a p-n junction, the radiative recombination is mainly confined to the interface region. The energy band diagrams are drawn based on the Anderson model. According to previous reports, the energy barrier heights for the electrons and holes near the interface between the n-ZnO and the p-GaN are estimated to be  $\Delta E_c$  = 0.15 eV and  $\Delta E_v = 0.12$  eV, respectively.<sup>31,32</sup> The barrier heights for electrons and holes are similar, but the hole mobility of p-GaN is much larger than the electron mobility of n-ZnO. Therefore, the ability of the electrons to drift from ZnO to GaN should be much weaker than that of the holes to drift from GaN to ZnO under forward bias as shown in Fig. 5a. As a result, most of the recombination occurs at the ZnO side, which could explain the strong ZnO NBE UV emission of n-ZnO/p-GaN under forward bias as shown in Fig. 3. In addition, the recombination at the interface and in p-GaN also contribute to the light emission. With an increase in the injection current, more holes would drift from GaN into ZnO, resulting in a giant enhancement of ZnO NBE UV emission. Fig. 5b shows the band diagram of the n-ZnO/p-GaN heterojunction under reverse bias. When a relatively low reverse bias is applied, the EL emission is dominated by the band-to-Mg-doped acceptor recombination in p-GaN and the defect-related recombination in ZnO. With the increase of the reverse bias, electron tunneling from the occupied valence band in p-GaN to the empty conduction band in n-ZnO is expected to occur due to the large energy band offset at the p-GaN/n-ZnO interface,33 and thus more radiative recombination would occur at the n-ZnO side at higher reverse bias. The interface states should play a major role for the tunneling process.



Fig. 5 The band diagram of the ZnO film/p-GaN heterojunction (a) under forward bias above the turn on voltage and (b) reverse bias.

## Conclusions

In summary, we have realized ultraviolet electroluminescence from a n-ZnO film/p-GaN heterojunction under both forward and reverse bias. Under forward bias, intense UV emission at  $\sim$  376 nm originating from ZnO rather than GaN can be observed accompanied by 408 nm interface emission from interface states, 430 nm light emission from GaN and visible light (520 nm) related to deep-level emission in ZnO. This phenomenon can be attributed to the larger hole mobility of p-GaN than the electron mobility of n-ZnO. More interestingly, when a reverse bias is applied on the device, the emissions at ~376 nm, ~408 nm, 430 nm and 520 nm can be still clearly observed. With the reverse injection current increasing, the intensity of ultraviolet electroluminescence increases dramatically and finally becomes dominant with the current larger than 20 mA. The electron tunneling from the occupied state in the valance band of GaN to the conduction band in n-ZnO is responsible for the reverse EL spectra. The results in this work will be helpful for the design of high efficiency n-ZnO/p-GaN heterojunction UV LEDs, which have potential application in the fields of solid-state lighting, panel displays, information storage, optical communication, and so on.

# Conflicts of interest

There are no conflicts to declare.

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