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Excitonic electroluminescence from ZnO-based heterojunction light emitting diodes

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Abstract

This work reports on the fabrication and characteristics of n-ZnO/p-GaN and n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction light emitting diodes (LEDs). Both devices exhibited diode-like rectifying current–voltage characteristics. Room temperature electroluminescence (EL) spectra for both LEDs consisted of dominant emission at 375 nm and two weaker bands centred at 415 nm and 525 nm, which were attributed to ZnO excitonic transition and defect-related emissions from GaN and ZnO, respectively. Moreover, it was demonstrated that the single heterojunction required a higher injection current to obtain an excitonic EL than that for the n-ZnO/n-MgZnO/n-ZnO/p-GaN LEDs. This indicated that the insertion of the MgZnO layer confined the injection carriers and thus increased the intensity of excitonic emission in the ZnO active region.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, with a band gap of 3.37 eV at room temperature (RT), has stimulated substantial interest in the quest for blue/ultraviolet light emitting diodes (LEDs) and laser diodes [1]. In contrast to other wide band gap semiconductors, ZnO has a large exciton binding energy of 60 meV, which ensures efficient excitonic lasing at RT [2]. Moreover, by alloying with MgO, the band gap of the $Mg_xZn_{1-x}O$ compound can be widened up to ∼4.0 eV [3]. However, the lack of reliable, high-quality p-type ZnO has hampered the development of ZnO homostructural LEDs, though much progress has been made in this field [4, 5]. Therefore, the unique properties of ZnO might be exploited by constructing heterojunction LEDs using ZnO as the active layer [6]. GaN-based compounds are considered promising candidates for the p-type layer because they have the same crystal structure (wurtzite), a small in-plane lattice mismatch (1.8% for GaN) and the same stacking sequence [6]. Thus, ZnO/GaN and related heterostructures have been widely reported [6–11]. Recently, Alivov *et al* compared n-ZnO/p-GaN and n-ZnO/p-AlGaN heterojunction LEDs [7, 8]. They showed that the electroluminescence (EL) emission at 430 nm originated from the GaN layer for the former and the EL peak at 389 nm from the ZnO layer for the latter [7, 8]. Several groups also reported the various emission wavelengths of the EL spectra (382 nm [9], 386 nm [10], 390 nm [11]), which were attributed to radiative recombination from the ZnO layer in their heterojunction LEDs. However, only one work demonstrated 375 nm EL from a ZnO/GaN/c-Al_2O_3 LED, which was assigned to the excitonic transition in the ZnO layer [6]. This work also demonstrates that it is

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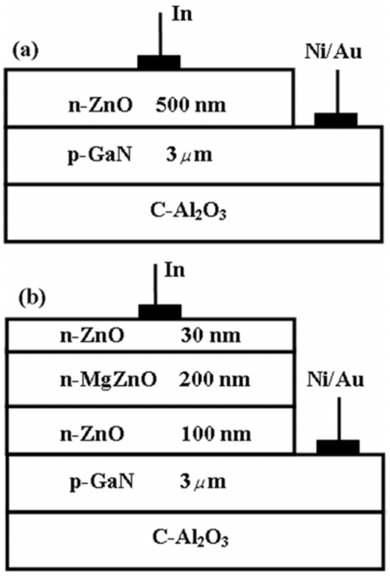

Figure 1. Schematic diagrams of n-ZnO/p-GaN (*a*) and n-ZnO/n-MgZnO/n-ZnO/p-GaN (*b*) heterojunctions.

possible to obtain significant hole injection from p-GaN into n-ZnO.

In this paper, we report on the fabrication and characteristics of n-ZnO/p-GaN and n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction LEDs. Both devices exhibit an excitonic EL under forward bias. Moreover, it is demonstrated that the intensity of excitonic emission in the ZnO active region can be enhanced by the insertion of an $Mg_{0.1}Zn_{0.9}O$ layer into heterojunctions.

2. Experimental details

Figure 1 shows schematic diagrams for two kinds of heterostructures involved here. Mg-doped p-type GaN films were grown on c-Al_2O_3 by metal organic chemical vapour deposition. ZnO and MgZnO films were grown by plasma-assisted molecular beam epitaxy (P-MBE). Pure Zn and Mg (99.9999%) were supplied by means of Knudsen effusion cells. O_2 (99.9999%) was introduced into an Oxford Applied Research Model HD25 rf (13.56 MHz) plasma source, operated at a power of 300 W. For the n-ZnO/p-GaN heterojunction, shown in figure 1(*a*), a 500 nm thick ZnO layer was grown on top of p-GaN at 800 °C. As shown in figure 1(*b*), an n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction was fabricated to confine the injected carriers in the ZnO active region. After the growth of a 100 nm thick ZnO layer on p-GaN at 800 °C, a 200 nm thick $Mg_{0.1}Zn_{0.9}O$ layer was grown as a barrier at 600 °C. Then, a 30 nm thick ZnO was grown for the n-type contact layer. All samples were cut into small pieces with an area of $3 \times 5\,mm^2$. Finally, ohmic contacts on p-GaN were formed by evaporating Ni/Au and subsequently annealing at 500 °C for 10 min in air. An indium electrode was sintered on a n-ZnO layer at 300 °C in vacuum. The unintentionally doped ZnO and MgZnO films exhibit n-type conductivity due to the native donor defects. The RT electrical properties of p-GaN, n-ZnO and n-$Mg_{0.1}Zn_{0.9}O$ were listed in table 1, which were performed by the Lakeshore 7707 Hall-effect measurement. RT EL spectra were collected under forward bias by a fluorescence spectrometer (LS-55, Perkin Elmer Co.). Photoluminescence (PL) spectra were measured employing a 325 nm He–Cd laser as the excitation source and collected with a microprobe system made by Jobin-Yvon Co.

Table 1. RT electrical properties of p-GaN, n-ZnO and n-$Mg_{0.1}Zn_{0.9}O$.

Samples	Resistivity (Ω cm)	Carrier concentration (cm^{-3})	Hall mobility ($cm^2\,V^{-1}\,s^{-1}$)
p-GaN	4.43	1.19×10^{17}	11.88
n-ZnO	7.89×10^{-2}	2.56×10^{18}	30.87
n-$Mg_{0.1}Zn_{0.9}O$	16.75	2.47×10^{17}	1.51

3. Results and discussion

In order to identify the electrical properties of the n-ZnO and n-$Mg_{0.1}Zn_{0.9}O$ layers in the heterostructures, we deposited a ZnO film (or a $Mg_{0.1}Zn_{0.9}O$ film) on the p-GaN and c-Al_2O_3 substrates simultaneously and estimated the electrical parameters of the layers in the devices by measuring the samples grown on c-Al_2O_3, respectively. Table 1 shows the RT electrical parameters of p-GaN, n-ZnO and n-$Mg_{0.1}Zn_{0.9}O$. The undoped ZnO films usually exhibit strong n-type conductivity. The nature of the dominant donors still remains controversial [12–15]. It is thought that the main sources of the unintentional n-type conductivity may be native defects (oxygen vacancies and zinc interstitials) [12,13], group-III elements (such as Al and Ga) [14] or hydrogen [15]. The $Mg_{0.1}Zn_{0.9}O$ film also exhibits n-type conductivity with the electron concentration of $2.47 \times 10^{17}\,cm^{-3}$.

Figure 2 shows the RT current–voltage (I–V) characteristics of the n-ZnO/p-GaN and n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunctions. Both devices exhibit a rectifying, diode-like behaviour, with turn-on voltages of 3–4 V and 4–5 V for the former and the latter, respectively. The Ni/Au contact to the p-GaN layer and the indium (In) contact to the n-ZnO layer show good ohmic behaviour, as shown in the inset of figure 2, confirming that the rectification arises from the p–n junction. Moreover, the turn-on is gradual and follows the I–V^2 relationship, which is expected for such wide band gap materials [6, 7]. By comparing the I–V characteristics of the two heterostructures, it can be observed that the insertion of $Mg_{0.1}Zn_{0.9}O$ results in a higher and soft turn-on voltage. The most possible reason is that the MgZnO layer increases the series resistance of the diode [9].

Figure 3(*a*) shows the RT EL emission from the n-ZnO/p-GaN heterostructure under a forward current of 20 mA. The EL spectrum consists of a strong peak at 377 nm and two weaker broad lines centred at 415 and 525 nm. To elucidate the origins of the EL emissions, the PL spectra of n-ZnO and p-GaN were measured at RT. As shown in figure 3(*b*), the PL spectrum of ZnO shows a strong ultraviolet emission at 375 nm (3.31 eV) with a weak deep-level (DL) emission around 525 nm. The 375 nm emission is tentatively

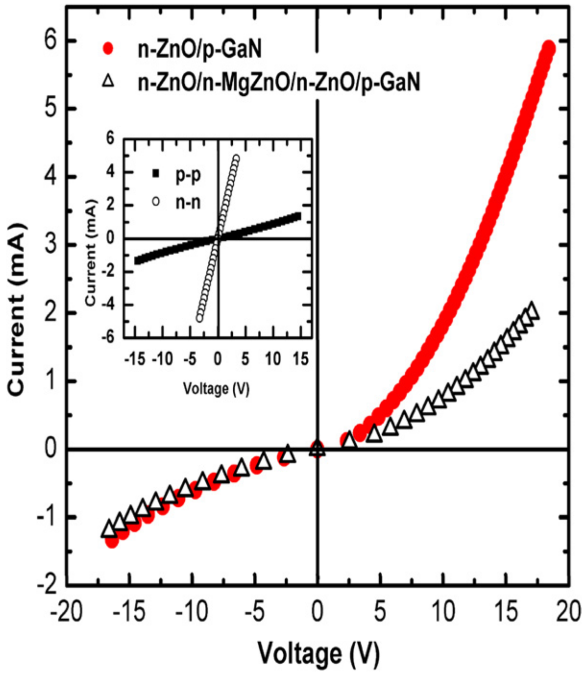

Figure 2. RT I–V characteristics of the heterojunction LEDs. The inset shows the I–V characteristics of Ni/Au and In ohmic contacts to p-GaN and n-ZnO layers, respectively.

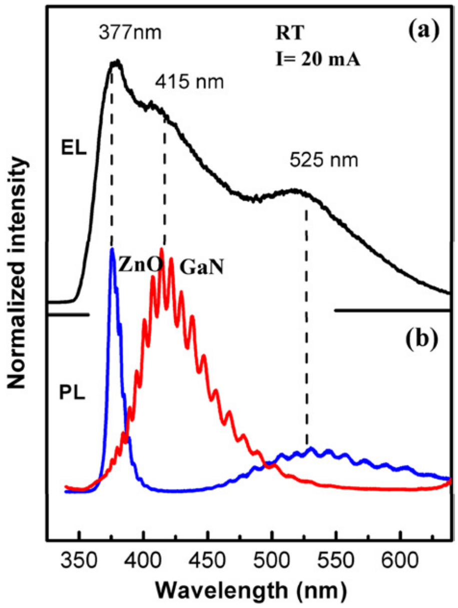

Figure 3. (*a*) RT EL spectrum of the n-ZnO/p-GaN heterojunction at the forward current of 20 mA. (*b*) RT PL spectra of p-GaN and n-ZnO.

attributed to the free exciton (FE) transition (this is elucidated below) and the DL band is known to be related to intrinsic defects such as O vacancy (V_O), Zn interstitial (Zn_i) and antisite defect O_{Zn} [16–18]. The PL spectrum of p-GaN shows only a broad emission centred at 415 nm with Fabry–Perot interference fringes [19]. This band was generally attributed to transitions from the conduction band or donors to Mg acceptor levels [7, 19].

In order to confirm the origin of the 375 nm emission at RT, the temperature-dependent PL spectra of the ZnO layer grown on p-GaN were measured, as shown in figure 4. At 80 K, the spectrum of the ZnO is dominated by an FE peak at 3.376 eV and a neutral donor-bound exciton (D°X) at 3.363 eV [20]. The weak emission peaks at 3.313 eV and 3.240 eV are attributed to the radiative recombination of the FE associated with the first and second longitudinal optical (LO) phonons, respectively [20]. The peak at 3.331 eV can be found at the higher energy side of the FE-1LO. However, the origin of this peak is not very clear although Meyer *et al* attributed the peak at 3.333 eV to excitons bound to structural defects (Y-line defect) [21]. As the temperature increases, the D°X peak quenches rapidly and the FE transition dominates the spectra up to RT. A Fabry–Perot interference fringe is also clearly observable in the PL signal. Thus, it is reasonable to conclude that the 375 nm (3.31 eV) emission peak in the RT PL spectrum of ZnO is attributed to the FE transition.

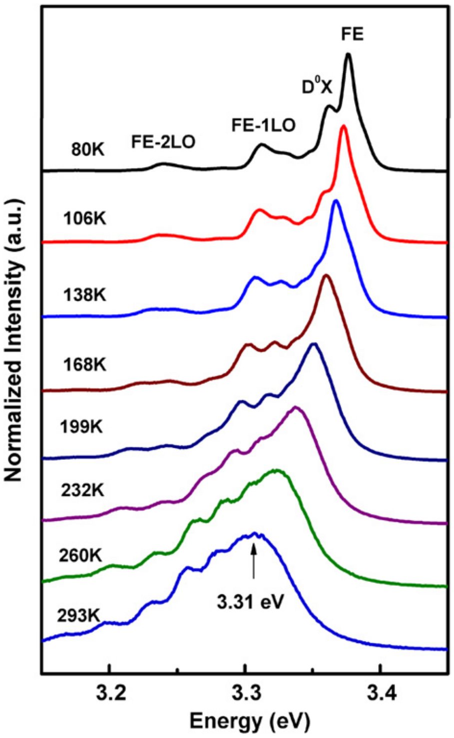

Figure 4. Temperature-dependent PL spectra of the ZnO film grown on p-GaN. The spectra were normalized and shifted vertically for clarity.

As seen in figure 3, three EL emission lines coincide very well with the PL peaks of n-ZnO and p-GaN, respectively. This indicates that strong excitonic EL is obtained from the ZnO region in the n-ZnO/p-GaN heterojunction LEDs, besides weak defect-related emissions in the GaN and ZnO layers. Furthermore, the coexistence of the emissions in GaN and ZnO demonstrates that when the holes inject from p-GaN into n-ZnO and radiatively recombine with electrons, the opposite process also occurs. This can be explained as follows. Based on the Anderson model, the conduction band offset is 0.15 eV while the valence band offset is 0.12 eV [9, 10], indicating that the energetic barrier for holes is somewhat less than the barrier for electrons. On the other hand, as shown in table 1, the carrier concentration in n-ZnO is larger than that in p-GaN, which results in the fact that electrons injection from

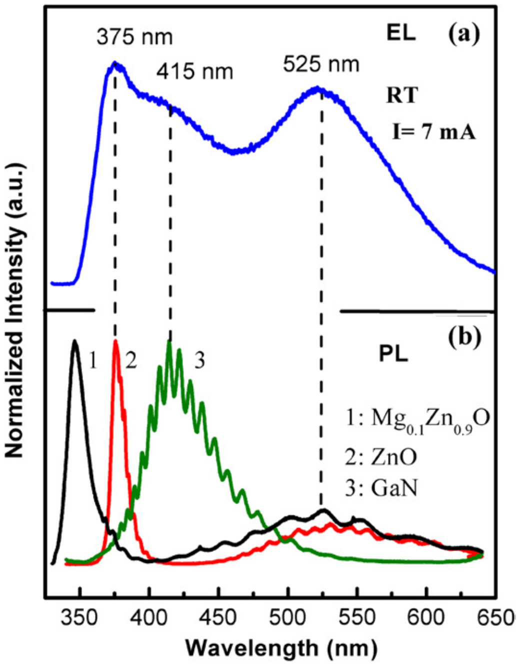

Figure 5. (*a*) RT EL spectrum of the n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction at the forward current of 7 mA. (*b*) RT PL spectra of n-$Mg_{0.1}Zn_{0.9}O$, p-GaN, and n-ZnO.

n-ZnO is more than holes injection from p-GaN. Therefore, radiative recombination occurs both in n-ZnO and p-GaN of the n-ZnO/p-GaN heterojunction.

Figure 5(*a*) shows the RT EL spectrum of the n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction LED at a forward current of 7 mA. As seen, the EL spectrum is dominated by 375 nm excitonic emission from the ZnO layer, although defect-related emissions from GaN and ZnO are also observed. As shown in figure 5(*b*), the PL spectrum of the n-$Mg_{0.1}Zn_{0.9}O$ film, grown under the same condition as in the LED, is presented. It consists of a strong ultraviolet emission at 346 nm (3.58 eV) and a weak DL emission around 525 nm. We expected that the injection carriers can be confined in the ZnO active layer by the insertion of such a n-$Mg_{0.1}Zn_{0.9}O$ layer into the heterojunction LEDs. Due to conduction band offsets, the $Mg_{0.1}Zn_{0.9}O$ layer forms a barrier of ∼100 meV for electrons injected into the ZnO active layer providing confinement [11]. And this confinement increases the carrier concentration in the active region and the probability of radiative recombination under forward bias. In contrast to this structure, carriers will be spread throughout the thick n-ZnO layer in the n-ZnO/p-GaN heterojunction [11].

The normalized EL spectra of the n-ZnO/p-GaN and the n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunctions LEDs, measured at the same injection current of 7 mA, are compared in figure 6. As expected, it can be clearly observed that the excitonic emission is much weaker for the former than that for the latter. As shown in figure 3, when the injection current increases to 20 mA, the excitonic emission dominates the EL spectrum of the n-ZnO/p-GaN LED. It is well known that the radiative recombination rate in a heterojunction is $R_{\mathrm{rad}} \propto Cnp$ [11], where C is the radiative recombination coefficient and n and p are the excess electron and hole concentrations near the p–n junction interface, respectively. Based on this relation, the increase in the forward current enhances the electron and hole concentrations, which increases the excitonic radiative recombination rate. Thus, the excitonic emission dominates the EL spectrum at the forward current of 20 mA. On the other hand, at the lower injection current (7 mA), the EL spectrum of the n-ZnO/p-GaN LED is dominated by defect-related emission. However, for the n-ZnO/n-MgZnO/n-ZnO/p-GaN structure, strong excitonic emission can be obtained at the same injection current (7 mA). It is believed that the insertion of an $Mg_{0.1}Zn_{0.9}O$ layer confines the injection carriers in the active region and thus increases the carrier density in the recombination zone [11, 22]. Additionally, it is expected that defect-related emissions in both the LEDs could be suppressed, even eliminated by further optimizing the device structure.

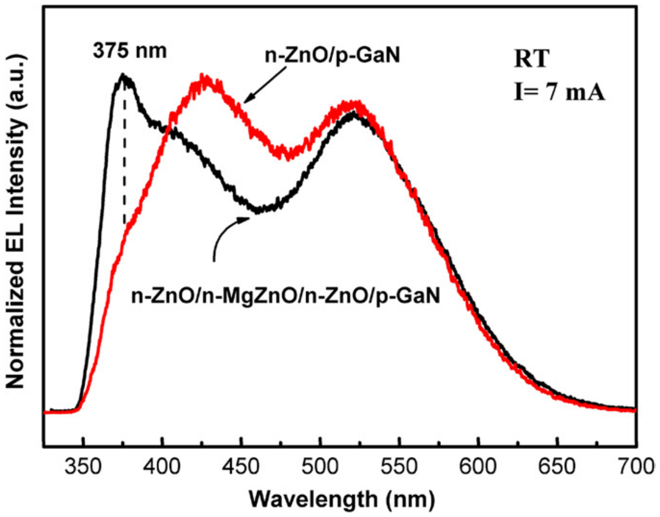

Figure 6. EL spectra of the n-ZnO/p-GaN and the n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction LEDs at the same injection current of 7 mA.

4. Conclusion

In conclusion, we fabricated n-ZnO/p-GaN and n-ZnO/n-MgZnO/n-ZnO/p-GaN heterojunction LEDs. Both devices exhibited rectifying, diode-like *I*–*V* characteristics, with turn-on voltages of 3–4 V and 4–5 V for the former and the latter, respectively. RT EL spectra for both the LEDs demonstrated strong ZnO excitonic emission, besides the defect-related emissions from the GaN and the ZnO layers. The results show that ZnO-based heterojunctions have great potential for application in ultraviolet LEDs, due to 60 meV exciton binding energy.

Acknowledgments

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