Improvement in electroluminescence performance of n-ZnO/Ga_2O_3/p-GaN heterojunction light-emitting diodes*

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n-ZnO/p-GaN heterojunction light-emitting diodes with and without a Ga_2O_3 interlayer are fabricated. The electroluminescence (EL) spectrum of the n-ZnO/p-GaN displays a single blue emission at 430 nm originating from GaN, while the n-ZnO/Ga_2O_3/p-GaN exhibits a broad emission peak from ultraviolet to visible. The broadened EL spectra of n-ZnO/Ga_2O_3/p-GaN are probably ascribed to the radiative recombination in both the p-GaN and n-ZnO, due to the larger electron barrier ($\Delta E_C = 1.85$ eV) at n-ZnO/Ga_2O_3 interface and the much smaller hole barrier ($\Delta E_V = 0.20$ eV) at Ga_2O_3/p-GaN interface.

Keywords: light-emitting diodes, heterojunction, ZnO

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1. Introduction

Due to the large direct band gap of 3.37 eV at room temperature (RT) and the high exciton binding energy of 60 mV, Zinc oxide (ZnO) has attracted considerable attention as a promising material for ultraviolet optoelectronic devices.[1,2] However, with great potential in electronic and photonic applications, there are few device applications of ZnO because it is a big problem to obtain high quality and stable p-type doping in ZnO. Thus, a heterojunction with an n-ZnO/p-GaN structure has been regarded as an alternative approach by virtue of their similarity in crystalline structure and closely matched lattice constant. Recently, many research studies on electroluminescence (EL) obtained from the n-ZnO/p-GaN heterojunction devices have been conducted.[3–8] However, the EL of the n-ZnO/p-GaN heterojunction light-emitting diode (LED) is emitted mainly from the p-GaN instead of the n-ZnO, with almost the same barrier height for electrons and holes. The origins of the EL emissions of n-ZnO/p-GaN heterojunction have been discussed by Alivov *et al.*,[3] which can be ascribed to the higher carrier concentration and mobility in n-ZnO. To improve the emission from ZnO and suppress the emission from GaN, some researchers employed wide band gap materials, such as MgO,[9] AlN,[10] SiO_2,[11] HfO_2,[12] and InGaN,[13] as the intermediate layer between ZnO and GaN to block the electron injection from ZnO. Due to the large conduction-band offsets (ΔE_C) in MgO/ZnO ($\Delta E_C = 3.55$ eV) and AlN/ZnO ($\Delta E_C = 3.29$ eV) interfaces, the interfacial layers can effectively block electrons injection from ZnO and the improved performances can be observed from n-ZnO/MgO/p-GaN[9] and n-ZnO/AlN/p-GaN LED.[10] However, these two structures also show high valence band offsets at MgO/GaN ($\Delta E_V = 0.90$ eV) and AlN/GaN ($\Delta E_V = 0.94$ eV) interfaces, which block the hole injection from p-GaN and lower the EL efficiency.

Alternatively, Ga_2O_3, with the modest direct band gap (4.9 eV), has outstanding physical and chemical properties including high thermal conductivity and high stability. The ΔE_V of p-GaN/Ga_2O_3 is roughly equal to 0.2 eV, much smaller than those of MgO/GaN ($\Delta E_V = 0.90$ eV) and AlN/GaN ($\Delta E_V = 0.94$ eV). Besides, the ΔE_C of n-ZnO/Ga_2O_3 is around 1.85 eV, which can effectively block electrons? injection from ZnO. Therefore, with Ga_2O_3 interlayer, the EL performance of n-ZnO film/p-GaN LEDs can be improved. In our previous study, a strong ultraviolet (UV) emission centered at 382 nm was obtained in an n-ZnO:Ga/p-GaN heterojunction LED due to the formation of Ga_2O_3 interfacial layers.[14] More recently, n-ZnO/Ga_2O_3/p-GaN heterojunction LED fabricated by MOCVD was reported by Liu *et al.*[15] and the device exhibited UV emission at 392 nm with a lower EL efficiency.

In the present work, Ga_2O_3 thin films are deposited on Mg doped p-GaN (p-GaN:Mg) by radio frequency (RF) sputtering and the ZnO films are then deposited on Ga_2O_3/GaN by pulsed laser deposition (PLD). Improved performance and blue shift phenomenon (from blue to UV) are revealed and the detailed electroluminescence mechanisms influenced by Ga_2O_3 layer are discussed.

2. Experiments

The schematic diagram of the n-ZnO/Ga_2O_3/p-GaN heterojunction LED structure is shown in Fig. 1(a). A

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4 mm×6 mm p-GaN:Mg/GaN/sapphire substrate (from the Inlead Technology Corporation, Taiwan) was chosen as the supporting substrate and a hole-injection layer was used for the LED. The p-GaN:Mg layers grown on GaN/sapphire by metal-organic chemical vapor deposition (MOCVD) each have a thickness of 1 μm, carrier concentration of 1.6×10^{17} cm^{-3}, and mobility of 14 cm^2/V·s. For the epitaxial growth of the n-ZnO/Ga_2O_3/p-GaN heterojunction structure, a 20-nm thick Ga_2O_3 layer was first deposited on p-GaN layer at 250 °C by RF sputtering with a Ga_2O_3 target in ambient Ar. Then, a 200-nm ZnO film was deposited on Ga_2O_3 layer using PLD technique, by ablating a ZnO target (99.999%) in the oxygen atmosphere (5 Pa) at 500 °C. A KrF excimer laser (COMPexPro 201, Coherent Inc.) was employed, operating with wavelength of 248 nm. The undoped ZnO films exhibited n-type conductivity with an electron concentration of 3.0×10^{18} cm^{-3} and a mobility of 20.4 cm^2/V·s. Finally, the Pt/Ti (30 nm/50 nm) and Pt/Ni (30 nm/50 nm) films were deposited on p-GaN and ZnO films by PLD as the electrodes, respectively. To achieve better Ohmic contact, the samples were annealed at 500 °C for 10 min.

Photoluminescence (PL) was excited by a 325-nm He-Cd laser (CVI Melles Griot) at room temperature (RT), while RT EL measurements were carried out with an ARS SP2557 monochromator. The crystalline regions of the films were characterized by X-ray diffraction (XRD) (Rigaku D/MAX2500V diffractometer with Cu K_α radiation). The *I*–*V* characteristics were investigated using a Keithley 2611A source meter.

3. Results and discussion

Figure 1(b) shows the *I*–*V* characteristics of heterojunction LEDs with and without the Ga_2O_3 intermediate layer. Both devices demonstrate a nonlinear rectifying behavior, while a small additional voltage drop is observed for the sample with the Ga_2O_3 layers. As illustrated in the inset of Fig. 1(b), the *I*–*V* characteristics show that good Ohmic contacts formed for Pt/Ni/p-GaN and Pt/Ti/n-ZnO, and consequently the rectifying behavior of the LED originates from the heterojunction.

Figure 2(a) shows the XRD pattern of n-ZnO/Ga_2O_3/p-GaN heterojunction device. As shown in the inset of Fig. 2(a), the ZnO (0002) peak and GaN (0002) peak are clearly observed. Moreover, two additional peaks at ∼ 33.68° and ∼ 71.44° are also found in the XRD pattern, which correspond to the Ga_2O_3 (111) and Ga_2O_3 (020) (JCPDS card No. 43-1012). The PL spectra of p-GaN substrate and n-ZnO grown on *c*-plane sapphire substrates are shown in Fig. 2(b). The PL spectrum of p-GaN film exhibits a broadened blue emission peak centered at 440 nm, which is generally attributed to the transitions from the conduction band or shallow donors to deep Mg acceptor levels.[16] The PL of ZnO film includes two emission bands. One is an intense near-band-edge (NBE) UV emission centered at 383 nm, and the other is a much lower deep-level emission band centered at 500 nm, which is due to the defect emission related to oxygen vacancies or zinc interstitials.[17]

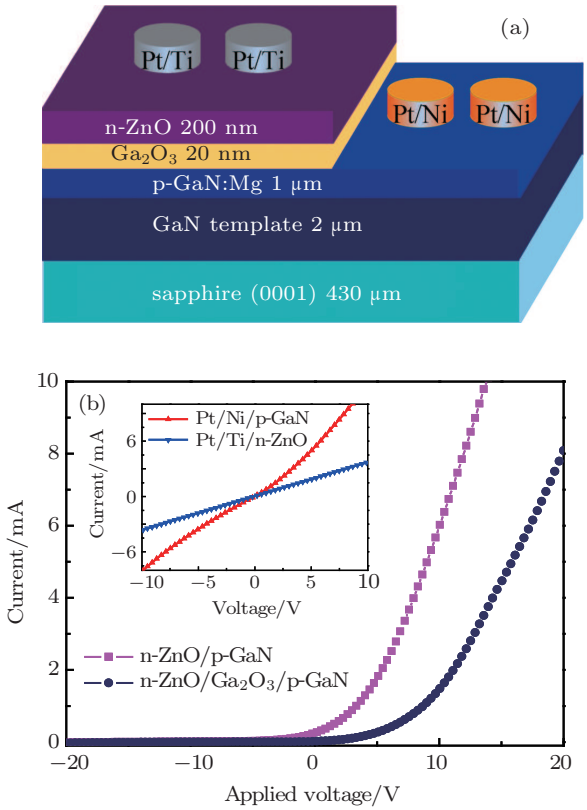


Fig. 1. (color online) (a) Schematic diagram of the n-ZnO/Ga_2O_3/p-GaN heterojunction device. (b) *I*–*V* curves of the LED device. The inset shows the Ohmic contact characteristics of Pt/Ni and Pt/Ti Ohmic contacts on p-GaN and ZnO.

The EL spectra of the n-ZnO/p-GaN and n-ZnO/Ga_2O_3/p-GaN heterojunction diodes with various currents are shown in Figs. 3(a) and 3(b), respectively. All the EL spectra are collected from the ZnO surface side of the devices at room temperature. As shown in Fig. 3(a), the EL spectra of the n-ZnO/p-GaN LED display one broadened emission band centered at about 430 nm. With injection current increasing to 6 mA, the emission peak position changes slightly, while the intensity of EL emission increases significantly. Compared with the PL spectra, the EL emission of n-ZnO/p-GaN LED can be clearly identified to originate from the deep level recombination in the p-GaN layer. The mechanism of radiative recombination in n-ZnO/p-GaN heterojunction LED has been widely investigated[3] and the recombination process can be understood by examining the energy band structure. As shown in Fig. 3(a), the ΔE_C and ΔE_V of ZnO/GaN interface are about 0.15 eV and 0.12 eV, respectively. Although the barrier heights for electrons and holes are almost the same, the electron injection from n-ZnO can prevail over the hole

injection from p-GaN, owing to the fact that the electron concentration and mobility in the n-ZnO films are higher than the hole concentration and mobility in the p-GaN layer. As a result, the radiative recombination mainly occurs in p-GaN instead of in n-ZnO.

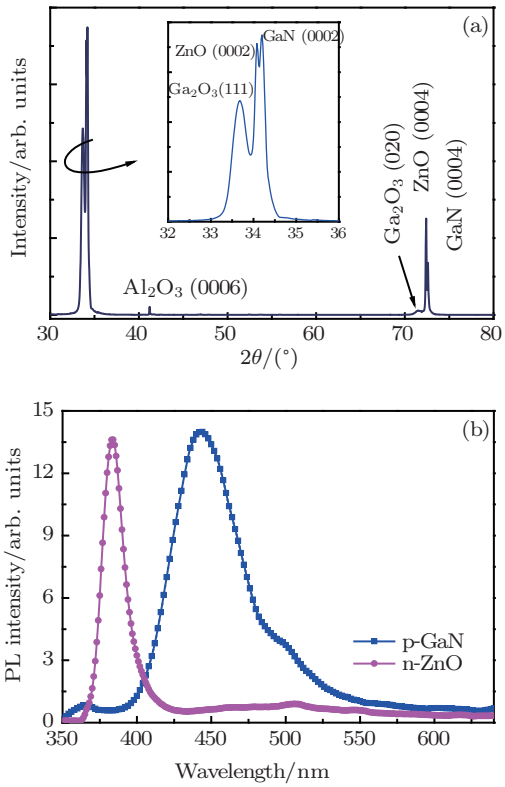


Fig. 2. (color online) (a) XRD pattern of the n-ZnO/Ga_2O_3/p-GaN heterojunction device, (b) PL spectra of p-GaN and n-ZnO films.

As shown in Fig. 3(b), the EL spectra of n-ZnO/Ga_2O_3/p-GaN heterojunction diode exhibits a broadened emission peak from ultraviolet to visible at different injection currents. As injection current increases from 0.5 mA to 10 mA, the intensity of the dominant emission peak increases and blue shift also appears. Peak-deconvolution with Gaussian function is applied to the EL spectrum at 10 mA. The result shows that the broadened spectrum consists of four distinct bands as shown in the inset of Fig. 3(b).

In order to understand the EL results of the n-ZnO/Ga_2O_3/p-GaN heterojunction LED better, each EL spectrum is split into four distinct sub-bands according to the Gaussian deconvolution above. As shown in the inset of Fig. 4(a), all the EL spectra consist of four subbands centered in a range of 380 nm–386 nm ("emission I"), 402 nm–420 nm ("emission II"), 427 nm–443 nm ("emission III") and 482 nm–488 nm ("emission IV"). Each subband corresponds to a particular recombination process, which will be elaborated on in the following.

Compared with PL spectra in Fig. 2(b), the UV emission band ("emission I") is attributed to the near band edge (NBE) emission in ZnO that originates from the recombination of free and bound excitons of ZnO, while the blue emission band ("emission III") is ascribed to the transitions from the conduction band or shallow donors to deep Mg acceptor levels in the p-GaN layer.[12,18,19] The violet emission ("emission II") is observed frequently in the EL spectra of ZnO-based hetero- and homojunctions, and is probably attributed to the transition from shallow donors to the valence band in ZnO.[9,12,18,19] Finally, the orange–green emission ("emission IV") matches well with the transition from a shallow donor level to the V_{Zn} level.[20]

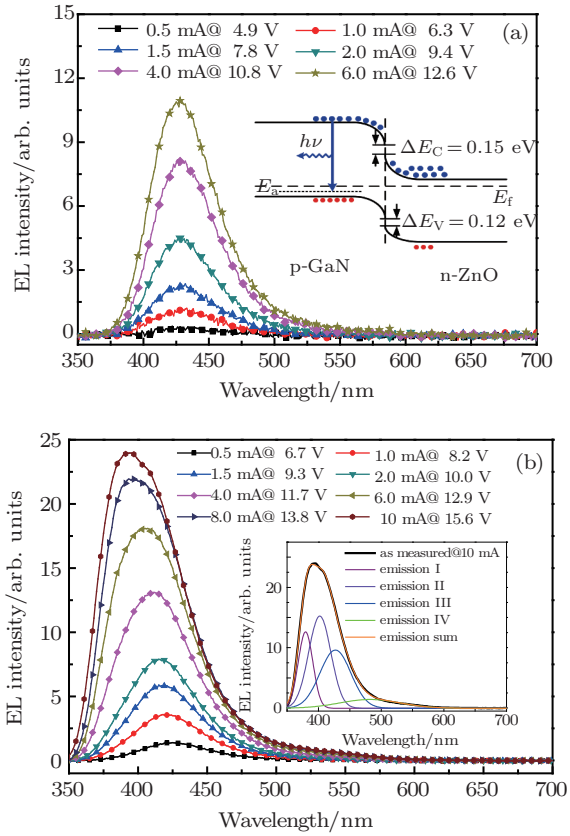


Fig. 3. (color online) (a) EL spectra of n-ZnO/p-GaN heterojunction LED. Inset shows the band diagram of the n-ZnO/p-GaN heterojunction. (b) EL spectra of n-ZnO/Ga_2O_3/p-GaN heterojunction LED. Inset shows the peak-deconvolution with Gaussian function of the EL spectrum at 10 mA.

The effect of the Ga_2O_3 intermediate layer on the EL results of the heterojunction can be understood in terms of the band alignment as illustrated in the inset of Fig. 4(a). To construct the band diagram, the bandgap and electron affinity energy of Ga_2O_3 is taken to be 4.9 eV and 2.5 eV,[21–23] respectively. For n-ZnO/p-GaN heterojunction with Ga_2O_3 intermediate layer, the ΔE_C for Ga_2O_3/ZnO is 1.85 eV while the ΔE_V for Ga_2O_3/GaN is 0.20 eV. Although ΔE_C for the Ga_2O_3/ZnO interface (1.85 eV) is much smaller than those of the MgO/ZnO and AlN/ZnO interfaces, the much smaller barrier height ($\Delta E_V = 0.20$ eV) for a hole can make hole injection from GaN to ZnO easier. As a result, the radiative

recombination can occur both in the p-GaN layer and in the n-ZnO layer simultaneously. Different results were found in Liu *et al.*'s report[15] and a single UV emission peak at 392 nm was observed in the n-ZnO/p-GaN heterojunction LED with a 70-nm-thick Ga_2O_3 electron blocking layers. Due to the large resistivity of Ga_2O_3 and thicker film layer, the significant internal heating takes place in the active region, which leads to the red shift of the peak wavelength.

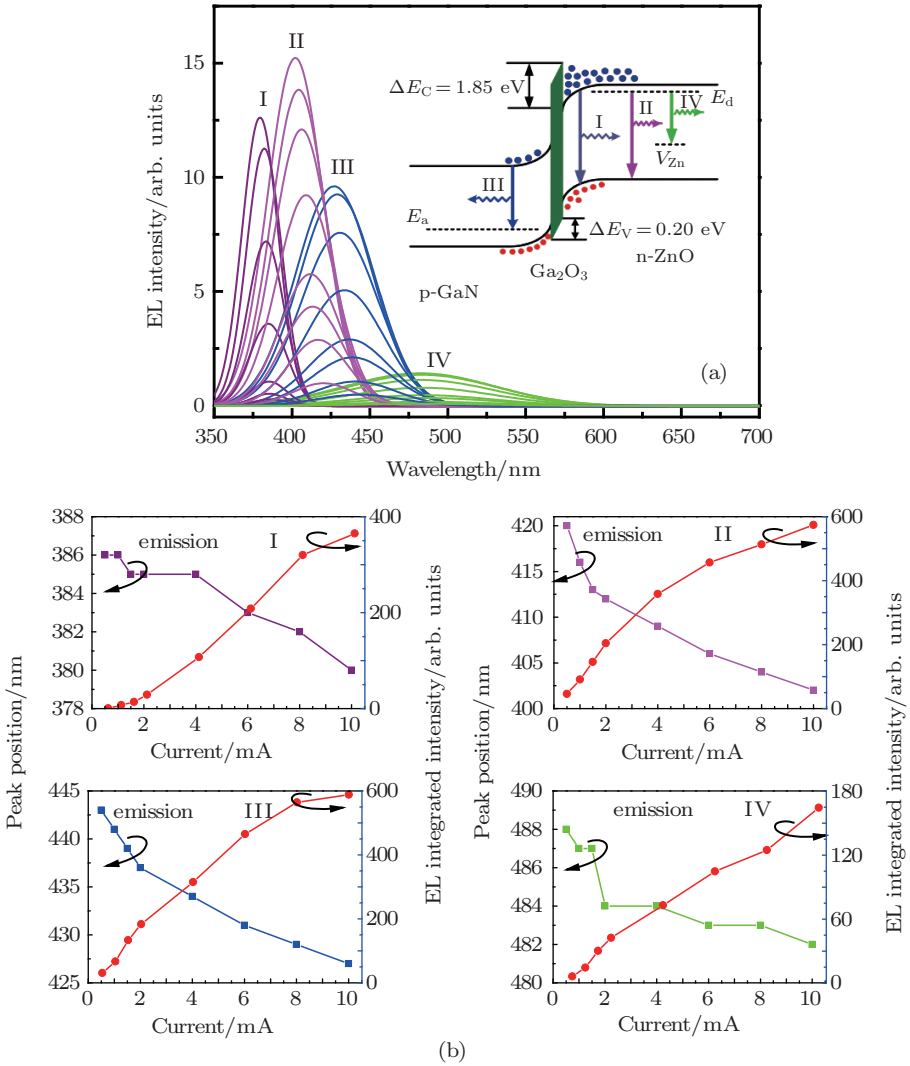


Fig. 4. (color online) (a) Gaussian deconvolution results for all EL spectra at different injection currents. Inset shows the energy band diagram of n-ZnO/Ga_2O_3/p-GaN heterojunction LED. (b) The plots of peak position and the corresponding intensity of the four sub-bands versus injection currents.

Figure 4(b) shows the plots of peak position and the corresponding intensity of the four sub-bands versus injection current. As the injection current increases, the intensities of all the four sub-bands increase and the blue shifts also augment. Obviously, the ZnO related emissions (emissions I and II) which lie in the UV spectrum region play dominant roles for the intensity of EL. Hence, the blue shift of the EL emission peak may come from two resources: the blue shift of sub-band positions and the change of relative intensities of the sub-bands at different injection currents.[18,19] When the forward bias is increased, the electrons and holes may possess higher kinetic energies, therefore the carriers have a much higher probability to go across the interface barrier and recombine in the p-GaN and n-ZnO layers. Due to the much smaller value of ΔE_V for the Ga_2O_3/GaN interface (0.20 eV) and the large value of ΔE_C for the Ga_2O_3/ZnO interface (1.85 eV), hole injection from p-GaN to n-ZnO is much easier than electron injection from n-ZnO to p-GaN. As a result, the intensity of the ZnO related emission increases faster than that of the GaN emission.

4. Conclusion

In this paper, n-ZnO/p-GaN and n-ZnO/Ga_2O_3/p-GaN heterojunction LEDs are fabricated. The EL performance is improved by inserting a thin Ga_2O_3 intermediate layer into n-ZnO/p-GaN interface, and using a much smaller barrier height

($\Delta E_V = 0.20$ eV) for a hole in Ga_2O_3/GaN interface. With Gaussian deconvolution analysis of the EL spectra, the origins of the broad emission are ascribed to four different electron–hole recombination processes.

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