ZnO-on-GaN heterojunction light-emitting diode grown by vapor cooling condensation technique

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The growth of ZnO-on-GaN heterostructures was implemented using the vapor cooling condensation system. The technique thus developed was employed to fabricate both the *p*-GaN/*n*-ZnO:In (*p*-*n*) and *p*-GaN/*i*-ZnO/*n*-ZnO:In (*p*-*i*-*n*) heterojunction light-emitting diodes (LEDs). A rectifying diodelike behavior was clearly observed from both the *p*-*n* and *p*-*i*-*n* heterojunction LEDs, with the forward turn-on voltage of 3 V and the reverse breakdown voltage of −15 V determined for the *p*-*n* heterojunction LEDs, compared to 7 and −23 V, respectively, for the *p*-*i*-*n* heterojunction LEDs. Based on the results of photoluminescence and electroluminescence studies conducted on these LED structures, the ZnO layer responsible for the peak emission wavelength of 385 nm were also verified experimentally. © *2007 American Institute of Physics*.
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Zinc oxide (ZnO) semiconductor is considered a promising material for advanced optoelectronic applications because it is a direct bandgap (3.37 eV) semiconductor with a large binding energy of 60 meV and a strong cohesive energy of 1.89 eV. Besides, ZnO semiconductor exhibits higher radiation hardness and amenability to conventional chemical wet etching. Recently, ZnO has increasingly become one of popular candidates for high temperature and highly transparent electron devices[1,2] and blue/ultraviolet optoelectronic devices.[3,4] Although highly conductive *n*-type ZnO can be obtained by relying on a proper doping with group III donor impurities,[5] *p*-type ZnO has instead been plagued by its irreproducibility and low quality.[6] Therefore, the homojunction ZnO structures have been seldom studied.[7] In view of the advantages of electronic and optical confinements offered by heterojunction structures, *n*-type ZnO has, thus, been frequently deposited on various *p*-type semiconductors.[8] By comparing with III-V nitride semiconductors, both GaN and ZnO share the same wurtzite structure and their lattice constants are nearly identical. Furthermore, because of a large bandgap discontinuity at heterointerface, ZnO/GaN and related heterostructures have, thus, been widely reported.[4,9–12] Various methods such as chemical vapor deposition,[10] sputter,[11] plasma-assisted molecular beam epitaxy,[12] molecular beam epitaxy,[13] and others have all been employed to grow ZnO/GaN heterostructures. In this work, a vapor cooling condensation method was used to deposit ZnO and In-doped ZnO (ZnO:In) films on *p*-type GaN. The electroluminescence (EL) of the resultant *p*-GaN/*n*-ZnO:In (*p*-*n*) and *p*-GaN/*i*-ZnO/*n*-ZnO:In (*p*-*i*-*n*) light-emitting diodes (LEDs) were observed and investigated.

In the vapor cooling condensation system, the material sources were put on a tungsten boat and heated. The sublimated material vapor gases were condensed and deposited on the substrate being cooled by liquid nitrogen. To investigate the quality of the deposited ZnO and ZnO:In films, those films were separately deposited on 1 μm thick Mg-doped GaN layer grown on *c*-plane (0001) sapphire substrates using a metalorganic chemical vapor deposition system. By activating the *p*-type dopant at 750 °C for 30 min in a N_2 ambient, the hole concentration and mobility of the Mg-doped GaN layer obtained were 3.7×10^{17} cm^{-3} and 10.8 cm^2/V s, respectively. By putting 0.85 g of ZnO powder on the tungsten boat, a 300 nm thick ZnO film was deposited on the cooled Mg-doped GaN in the vapor cooling condensation system. When Hall measurement was conducted at room temperature, the electron concentration and mobility of the deposited ZnO film were thereby obtained as 7.6×10^{15} cm^{-3} and 2.1 cm^2/V s, respectively. To deposit a 300 nm thick ZnO:In film on the Mg-doped GaN layer, 0.85 g of ZnO powder and 0.12 g of In were put together on the tungsten boat. The indium was placed underneath the ZnO powder on the tungsten boat. To analyze the composition of the ZnO:In film, an energy dispersive spectrometer (EDS) was used. The atomic ratio of 0.28, defined as In/(In+Zn), corresponding to the ZnO:In film was found. The EDS result indicated that the In was doped into the ZnO film. Furthermore, the electron concentration and mobility of the deposited ZnO:In were 1.7×10^{20} cm^{-3} and 3.7 cm^2/V s, respectively. The room temperature photoluminescence (PL) spectra of the *p*-GaN, *i*-ZnO, and *n*-ZnO:In films are shown in Fig. 1. The PL spectra were measured at room temperature using He–Cd laser ($\lambda=325$ nm) as excitation source. As seen from this figure, the PL spectrum of the *p*-GaN film consists of a broadband centered at a maximum wavelength (λ_m) of 432 nm. This broadband emission is a typical transition from the conduction band or shallow donors to the Mg acceptors.[14] For the PL spectrum of the *i*-ZnO film shown in Fig. 1, the ultraviolet emission with λ_m equals to 382 nm and a full width at half maximum of 13 nm can be attributed to the near-band edge (NBE) emission. For the PL spectrum of the *n*-ZnO:In film, the PL spectrum reveals a NBE UV emission at a shorter λ_m of 380 nm and a broad emission band centered at about 540 nm. The shorter λ_m of NBE emission

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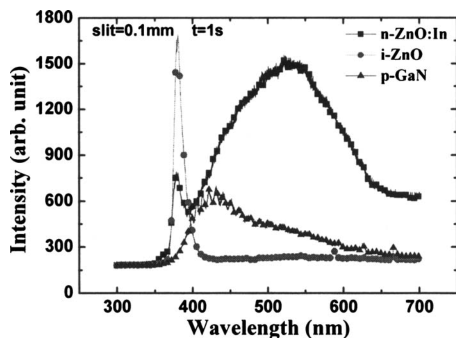

FIG. 1. The room temperature photoluminescence (PL) spectra of the *p*-GaN, *i*-ZnO, and *n*-ZnO:In films.

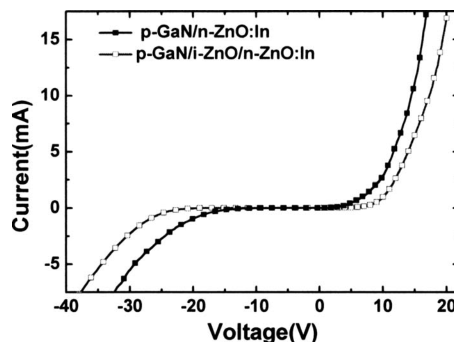

FIG. 3. The room temperature current-voltage characteristics of *p*-*n* and *p*-*i*-*n* heterojunction LEDs.

is attributed to the Burstein-Moss shift, which is related to the electron concentration. Moreover, the broad emission band is due to deep-level emission as induced by the oxygen vacancies in ZnO:In films.

Figures 2(a) and 2(b) show the schematic diagrams of the *p*-GaN/*n*-ZnO:In and *p*-GaN/*i*-ZnO/*n*-ZnO:In heterojunction LED structures. The room temperature current-voltage characteristics of *p*-*n* and *p*-*i*-*n* heterojunction LEDs were measured using an HP4145B semiconductor parameter analyzer and results are shown in Fig. 3. As seen in this figure, a rectifying diodelike behavior of the *p*-*n* and *p*-*i*-*n* heterojunction LEDs was clearly demonstrated. For the *p*-*n* heterojunction LEDs, the forward turn-on voltage and reverse breakdown voltage were 3 and −15 V, respectively, compared to 7 and −23 V, respectively, for the *p*-*i*-*n* heterojunction LEDs.

Figure 4 shows the room-temperature EL spectra of the *p*-*n* and *p*-*i*-*n* heterojunction light-emitting diodes. The EL spectra of the forward biased *p*-GaN/*n*-ZnO:In heterojunction consist of a broad emission band at 432 nm, which is attributed to the transition form the conduction band to the acceptor level ascribed to the Mg doped *p*-GaN when electrons are injected from the *n*-ZnO:In into the Mg-doped *p*-GaN.[14] By conducting the Hall measurement study on the *n*-ZnO:In and *p*-GaN layers, the carrier concentrations of *n*-ZnO:In and *p*-GaN are 1.7×10^{20} and 3.7×10^{17} cm^{-3}, respectively. It can be expected that the depletion region of the *p*-*n* heterojunction is mostly resided in the *p*-GaN region. Therefore, the radiative recombination occurs mainly at the *p*-GaN region. On the other hand, the EL emission is emitted from ZnO, when undoped *i*-ZnO layer is inserted between *n*-ZnO:In and *p*-GaN to form *p*-*i*-*n* heterostructure LEDs. Because the ZnO layer has the lowest carrier concentration of 7.6×10^{15} cm^{-3} compared with that of the *n*-ZnO:In and the *p*-GaN layers, hence, the holes from *p*-GaN and electrons from *n*-ZnO:In are thereby injected into the ZnO layer to undergo the radiative recombination. As different from the EL spectrum of the *p*-*n* heterojunction (*p*-GaN/*n*-ZnO:In) LEDs, the EL peak of *p*-*i*-*n* heterojunction (*p*-GaN/*i*-ZnO/*n*-ZnO:In) LEDs is located instead at 385 nm, which overlaps with the peak wavelength of the *i*-ZnO PL spectrum as shown in Fig. 1. Based on the EL spectrum of *p*-*i*-*n* LEDs obtained, the EL emission of *p*-*i*-*n* LEDs is therefore identified as originating from the *i*-ZnO film.

In conclusion, both *p*-GaN/*n*-ZnO:In and *p*-GaN/*i*-ZnO/*n*-ZnO:In heterojunction light-emitting diodes were fabricated. By implementing the *p*-*i*-*n* heterojunction structure, the radiative recombination was expected to take place in the *i*-ZnO region. Experimentally, the observed UV EL peak of 385 nm, which was related to ZnO exciton recombination, was evidently attributed to the *p*-*i*-*n* hetero-

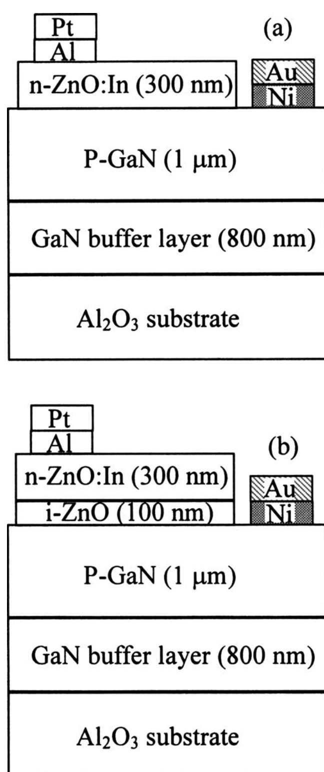

FIG. 2. The schematic diagrams of (a) *p*-GaN/*n*-ZnO:In and (b) *p*-GaN/*i*-ZnO/*n*-ZnO:In heterojunction LEDs structures.

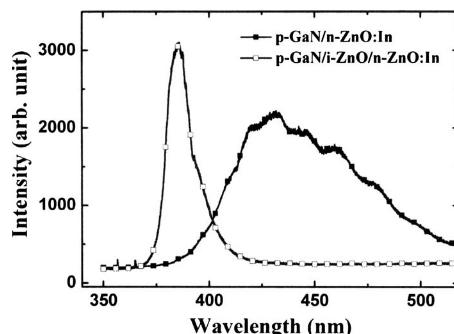

FIG. 4. The room-temperature electroluminescence (EL) spectra of the *p*-*n* and *p*-*i*-*n* heterojunction light-emitting diodes.

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structure involved. Due to the higher exciton binding energy of ZnO as grown by vapor cooling condensation, the *p-i-n* heterostructure thus developed has one of potential applications in UV LEDs for high-temperature operation.

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