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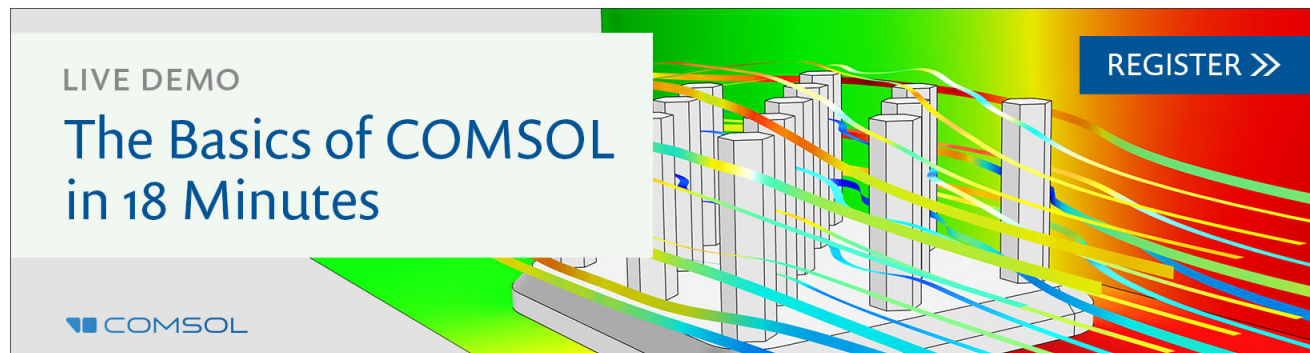
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***p*-ZnO/*n*-GaN heterostructure ZnO light-emitting diodes**

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We report on the characteristics of a ZnO light-emitting diode (LED) comprised of a heterostructure of *p*-ZnO/*n*-GaN. The LED structure consisted of a phosphorus doped *p*-ZnO film with a hole concentration of $6.68 \times 10^{17} \text{ cm}^{-3}$ and a Si-doped *n*-GaN film with an electron concentration of $1.1 \times 10^{18} \text{ cm}^{-3}$. The *I*-*V* of the LED showed a threshold voltage of 5.4 V and an electroluminescence (EL) emission of 409 nm at room temperature. The EL emission peak at 409 nm was attributed to the band gap of *p*-ZnO which was reduced as the result of the band offset at the interface of *p*-ZnO and *n*-GaN. © 2005 American Institute of Physics.

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Many of the physical properties of ZnO and GaN are similar.¹ For example, ZnO and GaN both have wurtzite crystal structures, almost the same in-plane lattice parameter (the lattice mismatch $\sim 1.8\%$), and a room temperature band gap of 3.3 and 3.4 eV, respectively. In addition, ZnO has several advantages, which include a large exciton binding energy ($\sim 60 \text{ meV}$ vs 26 meV for GaN), a higher radiation hardness, amenability to wet chemical etching, the availability of large area ZnO substrates, and relatively low materials costs.² Therefore, ZnO is very attractive for blue/UV optoelectronics and high temperature/transparent electronics. However, ZnO has suffered from the lack of reproducible and high quality *p*-type material. As a result, only a very few studies have been reported regarding the homojunction ZnO light-emitting diodes (LEDs). Ryu *et al.* reported only on diode characteristics but not on the emission characteristics.³ Guo *et al.* and Aoki *et al.* reported on the diode characteristics and broad range emission but the performance of the LEDs used in their study were very poor.^{4,5} Since heterostructure-based LEDs would be expected to exhibit improved current confinement compared to a homojunction LED, heterojunction LEDs have been constructed by depositing *n*-ZnO or *n*-MgZnO on various *p*-type semiconductor layers such as ZnTe, Cu₂O, SrCu₂O₂, GaN, and AlGaIn.⁶⁻¹¹ However, a heterojunction LED with a heterostructure of *p*-ZnO/*n*-GaN has not been examined due to the lack of *p*-ZnO. We recently reported on the growth of stable *p*-ZnO thin films with a high hole concentration, produced by sputtering a ZnO target mixed with P₂O₅ at high temperatures followed by a rapid thermal annealing (RTA) process.¹²

In this study, we report on the growth and device properties of *p*-ZnO/*n*-GaN heterojunction LEDs. The electroluminescence (EL) emission in the blue-violet region was observed from the *p*-ZnO/*n*-GaN heterojunction LED at forward bias voltages. The EL emission and the *I*-*V* measurement confirmed that the phosphorus doped *p*-ZnO layer has a sufficiently high hole concentration to form a *p*-*n* junction for ZnO UV LED application.

A schematic diagram of the *p*-ZnO/*n*-GaN heterojunction LED is shown in Fig. 1. A Si-doped GaN layer was grown on a sapphire substrate in a metalorganic chemical

vapor deposition system using trimethylgallium, ammonia, and monosilane as the source materials for Ga, N, and Si, respectively. The sapphire substrate was preheated in a stream of H₂ at 1030 °C for 3 min, on which a 25-nm-thick GaN buffer layer had been grown at 560 °C. This was followed by the growth of a 1.6- μm -thick Si-doped GaN epilayer at 1020 °C. The electrical properties of the *n*-GaIn film were examined at room temperature by Hall effect measurements using the Van der Pauw configuration. The electron carrier concentration and mobility were $1.2 \times 10^{18} \text{ cm}^{-3}$ and $200 \text{ cm}^2/\text{V s}$, respectively. After the growth of the Si-doped GaN layer, the sample was transferred to a rf-magnetron sputtering chamber to grow a phosphorus doped ZnO (ZnO:P) layer. A 0.01 wt % P₂O₅ mixed ZnO target with a 2 in. diameter and a plasma comprised of a mixture of Ar and O₂ with a gas flow ratio (1:3) were used to deposit the ZnO:P films. The ZnO:P film with a thickness of 0.4 μm was deposited at a substrate temperature of 500 °C. The ZnO:P films were subjected to a RTA process at a temperature above 800 °C under a N₂ ambient atmosphere, to activate the *p*-type dopants. The hole concentration and mobility were $6.68 \times 10^{17} \text{ cm}^{-3}$ and $1.37 \text{ cm}^2/\text{V s}$, respectively. The heterojunction ZnO LED with a size of $300 \times 300 \mu\text{m}$ was fabricated using a 3% HCl aqueous solution to etch out the *p*-ZnO layer to expose the *n*-GaIn layer for an *n* electrode. Ohmic contacts to the *n*-GaIn and *p*-ZnO were made of Ti/Al (30/80 nm)¹³ and NiO/Au (30/50 nm), respectively. The metal layers were deposited by electron beam evaporation and annealed at 500 °C for 30 s under N₂ by a RTA process.

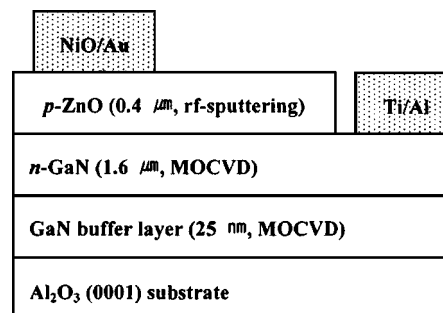


FIG. 1. Schematic diagram of the *p*-ZnO/*n*-GaIn heterojunction ZnO LED structure.

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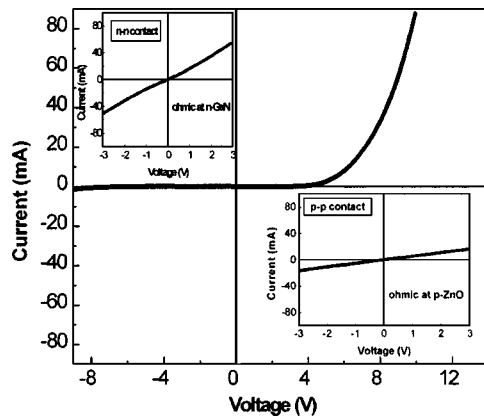


FIG. 2. The I - V characteristics of p -ZnO/ n -GaN heterostructure illustrating the rectifying behavior. The inset shows the I - V characteristics of Ti/Al and NiO/Au metal contacts on n -GaN and p -ZnO films. The I - V in the inset shows Ohmic contact characteristics.

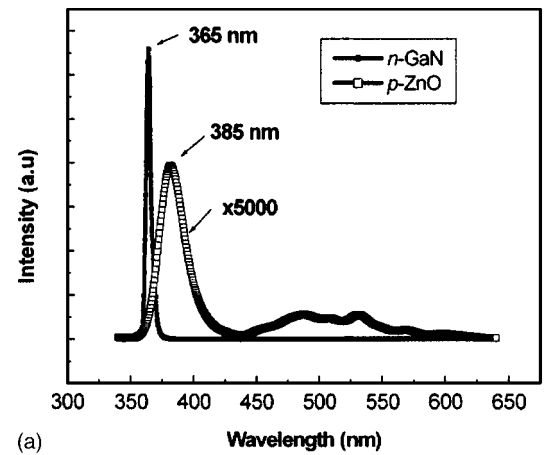
Photoluminescence (PL) measurements of p -ZnO and n -GaN layers were performed at room temperature using a He-Cd laser operating at 325 nm. The I - V and EL of the p -ZnO/ n -GaN LED were measured at room temperature using a semiconductor parameter analyzer (HP 4155A).

The inset of Fig. 2 shows the I - V characteristics of the Ti/Al and NiO/Au metal contacts on n -GaN and p -ZnO films, respectively, indicating that good Ohmic contacts are formed on both electrodes. These results show that the rectifying characteristics shown in Fig. 2 are due to the heterojunction of the p -ZnO/ n -GaN LED and not to semiconductor/metal contacts. The I - V characteristics of the fabricated heterostructure at room temperature are shown in Fig. 2. As shown in Fig. 2, the I - V characteristic of the p -ZnO/ n -GaN heterostructure shows the characteristics of a nonlinear and rectifying diode. It also shows a threshold voltage of 5.4 V and a low leakage current of 2×10^{-4} A.

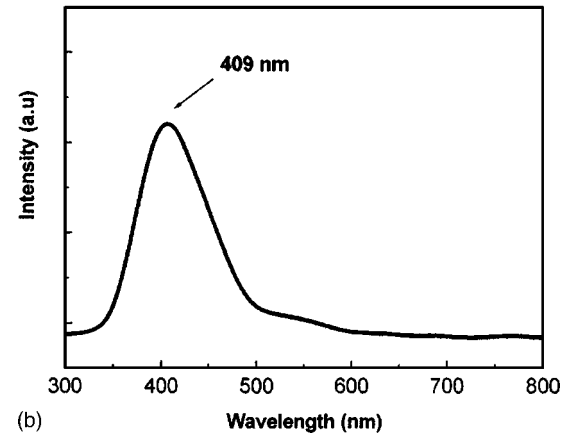
The PL spectra of the p -ZnO and n -GaN films observed at room temperature are shown in Fig. 3(a). The PL spectrum of p -ZnO shows a near-band-edge (NBE) emission at 385 nm and a broad defect-related green band at 500 nm. The PL spectrum of the n -GaN film shows an intense NBE emission at 365 nm, which can be attributed to a transition from the valence band to a shallow Si donor level.¹⁴ The p -ZnO/ n -GaN LED showed a blue-violet EL spectrum with a peak emission at 409 nm as shown in Fig. 3(b). The EL emission at an input current of 40 mA was too weak to be measured by an optical power meter, but it could be seen by the naked eye in a darkened room.

A comparison of the EL spectrum of the LED with the PL spectra of p -ZnO and n -GaN, as shown in Fig. 3(a), indicates that the origin of the EL emission is the p -ZnO region of the LED.

The difference in the emission peaks between the EL peak at 409 nm and the PL peak at 385 nm of p -ZnO can be explained by the energy band diagram of p -ZnO/ n -GaN, as shown in Fig. 4. Figure 4 shows the “ideal” heterojunction band diagram for p -ZnO/ n -GaN, which was constructed by following the Anderson model.¹⁵ To construct the band diagram, the electron affinities (χ) of ZnO and GaN were assumed to be 4.35 eV (see Ref. 16) and 4.2 eV,¹⁷ respectively. The band gap energies (E_g) are 3.37 and 3.39 eV, respectively, for ZnO and GaN at room temperature. As shown in the energy band diagram, the energy barrier ΔE_c for an elec-



(a)



(b)

FIG. 3. (a) PL spectrum of n -GaN and p -ZnO layers at room temperature and (b) an EL spectrum of p -ZnO/ n -GaN heterostructure at an injection current of 60 mA.

tron is $\Delta E_c = \chi(\text{GaN}) - \chi(\text{ZnO}) = 4.2 - 4.35 = -0.15$ eV, and the energy barrier ΔE_v for a hole is $\Delta E_v = E_g(\text{GaN}) + \Delta E_c - E_g(\text{ZnO}) = 3.39 - 0.15 - 3.37 = -0.13$ eV. Thus, there are two energy band offsets due to the different electron affinities and the band gaps between ZnO and GaN. Electrons and holes can accumulate at the interface due to the conduction and valence band offsets, as shown in Fig. 4. Figure 4 shows that the recombination of holes and electrons occurs in the p -ZnO region and the EL peak from p -ZnO would be expected to appear at 404 nm rather than 385 nm due to the band offset of 0.13 eV at the valence band of p -ZnO. The estimated

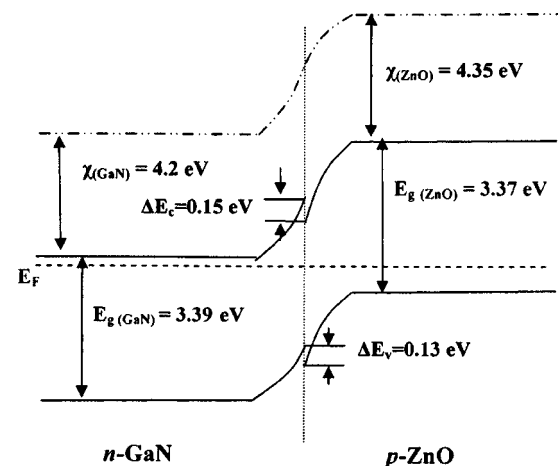


FIG. 4. Energy band diagram of the p -ZnO/ n -GaN heterojunction LED.

value of 404 nm is very close to the observed EL peak at 409 nm. The EL emission from *p*-ZnO rather than *n*-GaN is very plausible since the carrier mobility of *n*-GaN (200 cm²/V s) is very high compared to the carrier mobility of *p*-ZnO (1.37 cm²/V s). These results show that it is possible to fabricate an UV emission ZnO LED using a *p*-ZnO/*n*-GaN heterostructure. The diode *I*-*V* characteristic and the EL emission from the *p*-ZnO/*n*-GaN heterojunction LED also confirm that *p*-ZnO can be grown by doping the ZnO with phosphorus oxide.

In conclusion, the findings herein demonstrate that a *p*-ZnO/*n*-GaN heterojunction ZnO LED can be successfully formed on a *c*-plane sapphire substrate. The LED with *p*-type ZnO showed a diode *I*-*V* characteristic and an EL emission of 409 nm which corresponds to the band gap of *p*-ZnO grown on *n*-GaN.

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