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In this work, we report on the growth, fabrication, and device characterization of wide-band-gap heterojunction light-emitting diodes based on the n-ZnO/p-GaN material system. The layer structure is achieved by first growing a Mg-doped GaN film of thickness 1 μm on $Al_2O_3(0001)$ by molecular-beam epitaxy, then by growing Ga-doped ZnO film of thickness 1 μm by chemical vapor deposition on the p-GaN layer. Room-temperature electroluminescence in the blue-violet region with peak wavelength 430 nm is observed from this structure under forward bias. Light–current characteristics of these light-emitting diodes are reported, and a superlinear behavior in the low current range with a slope 1.9 and a sublinear behavior with a slope 0.85 in the high current range are observed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1615308]

ZnO and GaN are similar materials in many of their physical properties.[1] For example, ZnO and GaN both have wurtzite crystal structures, almost the same in-plane lattice parameter (the lattice mismatch ~1.8%), and room-temperature band gaps of 3.3 eV and 3.4 eV, respectively. At the same time, ZnO has some substantial advantages over GaN, the wide-band-gap semiconductor currently utilized in the short-wavelength optoelectronics industry. Some of these advantages include a larger exciton binding energy (~60 meV versus 26 meV for GaN), a higher radiation hardness, simplified processing due to amenability to conventional chemical wet etching, and, most significantly, the availability of large area substrates at relatively low material costs.[2] Currently, however, ZnO suffers from the lack of a reproducible, high-quality, p-type epitaxial growth technology. Although much progress has been made in this area,[3–5] the fabrication of effective ZnO-based light-emitting diodes (LEDs) and laser diodes must await further development of good, reproducible, p-type material. Currently, however, several groups have demonstrated good-quality p-type GaN (p GaN). Based on their similar materials properties, and the relative availability of p GaN, we explored the growth and fabrication of devices combining n ZnO with p GaN. One further advantage of ZnO/GaN LEDs is that heterostructure-based devices exhibit improved current confinement compared to homojunctions, which leads to higher recombination and improved device efficiency. The heteroepitaxial combination of GaN

with ZnO has been reported previously in literature.[6–8] However, while researchers were growing ZnO on GaN, the GaN films were n type in all of these reports, and served primarily as a buffer layers for obtaining high-quality ZnO layers due to their close lattice parameters. Presently, there have been no reports on the growth of n ZnO films on p-type GaN, or of fabricating devices from this heteroepitaxial materials system. In this letter, we report on the growth and device properties of n-ZnO/p-GaN heterojunction LEDs. Electroluminescence (EL) in the blue-violet region was observed under forward bias.

A schematic diagram of the n-ZnO/p-GaN heterojunction LED structure is shown in Fig. 1. For the epitaxial growth of this structure, we begin with p-type GaN doped with Mg having a thickness of 1.0 μm. This was grown on $Al_2O_3(0001)$ substrates by molecular-beam epitaxy using ammonia as the nitrogen source, and Knudsen cells for both the Ga and Mg. The substrate temperature during growth was 800 °C as determined by an optical pyrometer operating with a central wavelength of 1 μm and an emissivity setting of 0.3. The growth rate was 0.8 μm/h^{-1}. After growth of the GaN:Mg layer, the sample was removed to atmosphere, and then loaded into a separate chamber for growth of the ZnO layer. The n-type ZnO layer was grown using a chemical vapor deposition method to a thickness of 1.0 μm. The details of this method are given in Ref. 9. We use Ga, a group-III element, as our donor dopant species. This has been found to be a good approach for growing n-type ZnO (Refs. 10 and 11) where Ga incorporates substitutionally on the Zn sites of the lattice, forming a donor level with activation energy of

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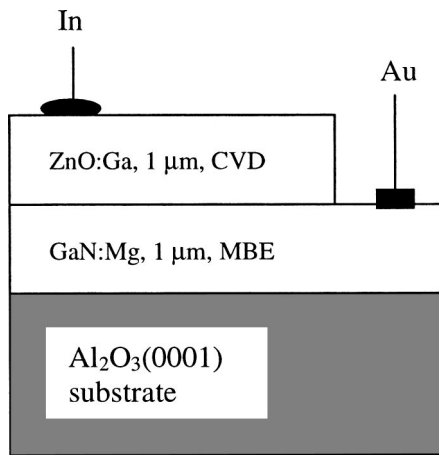[b)]Electronic mail: joseph.vannostrand@wpafb.af.mil

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

FIG. 2. RT CL spectra of (a) ZnO:Ga and (b) GaN:Mg films.

$\sim$50 meV.[12] The electrical properties of films of both GaN and ZnO films grown under similar conditions were measured at room temperature (RT) by Hall effect using the four-point van der Pauw configuration, and the free carrier concentration and mobility were found to be $p = 3.5 \times 10^{17}$ cm^{-3} and $\mu_p = 10$ cm^2 V^{-1} s^{-1} for acceptors in GaN:Mg, and $n = 4.5 \times 10^{18}$ cm^{-3}, and $\mu_n = 40$ cm^2 V^{-1} s^{-1} for donors in ZnO:Ga.

The heterojunction devices were fabricated by first masking the surface, then using a 10% HNO$_3$ aqueous solution to etch away the n-ZnO layer down to the p-GaN layer through a 2×2 mm^2 opening in the mask. This technique exploits the property that ZnO etches rapidly in acid, while GaN is very resistive to these environments. Ohmic contacts to the n ZnO were made by applying indium (In) with a soldering iron, and to the p GaN by thermal deposition of gold (Au). Current–voltage ($I–V$) characteristics of the area between two In–In and two Au–Au points of the ZnO:Ga and GaN:Mg layers, respectively, were measured and good ohmic contacts were observed. For comparison, isotype n-ZnO/n-GaN heterostructures were also grown under the same conditions as the anisotype n-ZnO/p-GaN heterostructures. The $I–V$ characteristics of the heterostructures were measured using an oscillograph adapted for this purpose. EL measurements were performed under dc-biased conditions at RT and at different injection currents. Optical properties of the ZnO and GaN films were explored using cathodoluminescence (CL) spectroscopy at RT, using an electron accelerating voltage of 20 keV and an electron-beam current range 0.1–1 μA.

The CL spectra of the ZnO and GaN layers are presented in Figs. 2(a) and 2(b), respectively. As can be seen from Fig. 2, the CL spectrum of the ZnO film [Fig. 2(a)] consists of intense, near-band-edge (NBE), ultraviolet emission with a wavelength maximum (λ_{max}) at 390 nm and a full width at half maximum (FWHM) of 118 meV. A broad defect-related green band with much lower intensity near $\lambda_{max} \sim 510$ nm, having a FWHM of 330 meV, is also shown in Fig. 2. In contrast, the CL spectrum of the GaN:Mg film [Fig. 2(b)] consists of a weak NBE band with λ_{max} at 383 nm, and of a more intense broadband with λ_{max} at 430 nm. This is typical of Mg-doped GaN films, and is generally attributed to tran-
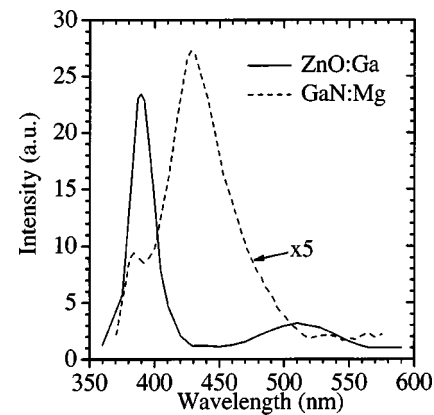
sitions from the conduction band or shallow donors to deep Mg acceptor levels.[13,14]

The $I–V$ characteristics of the fabricated heterostructure at RT are presented in Fig. 3. As shown in Fig. 3, the $I–V$ characteristics of the n-ZnO/p-GaN heterostructure are that of a nonlinear, rectifying diode [Fig. 3(a)]. The built-in voltage under forward bias is $\sim$3 V, although the turn on appears very soft. We also observe a leakage current of $\sim$5 $\times 10^{-6}$ A, and a relatively low reverse bias breakdown voltage of $\sim$$-3$ V. In contrast to this, the $I–V$ characteristics of the n-ZnO/n-GaN heterostructure are found to be ohmic and nearly linear [Fig. 3(b)]. Based on these results, we conclude that the rectifying diodelike behavior of the n-ZnO/p-GaN junction results from the electrical nature of components of the n-p heterojunction, rather than from some interface or contact-related phenomena. Further, an $\sim I–V^2$ relationship, as is expected for wide-band-gap materials, like ZnO, GaN, and SiC,[15–17] is observed over a wide forward bias range [Fig. 3(b)]. The physical basis of the $I–V^2$ relationship is attributed to space-charge limited current,[15–17] although there is some continuing debate on this subject.[17] The relatively low threshold voltage of our n-p heterostructure ($\sim$3 V), as well as the low reverse bias breakdown voltage, are probably due to defects in the materials, especially extended defects in the GaN because of the large lattice mismatch between GaN and sapphire ($\sim$16%).

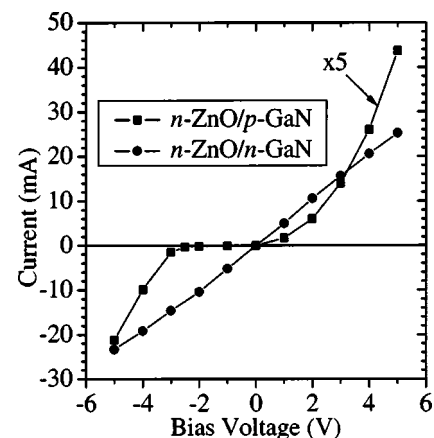EL emission of the n-ZnO/p-GaN heterostructure was observed under forward bias and is shown in Fig. 4. As

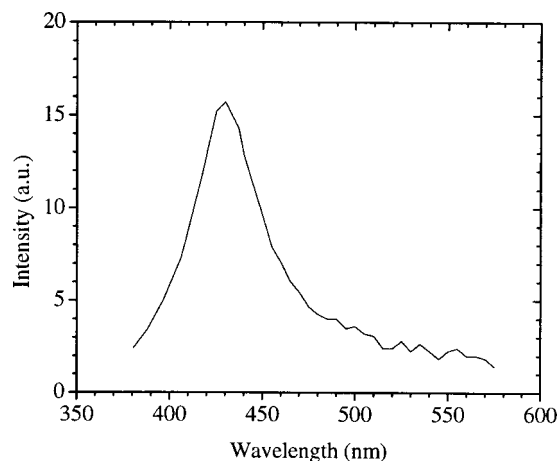FIG. 3. $I–V$ characteristics of (a) n-ZnO/p-GaN and (b) n-ZnO/n-GaN heterostructures. Positive voltage indicates forward bias.

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FIG. 4. EL spectrum of an n-ZnO/p-GaN heterostructure.

FIG. 5. RT $L-I$ characteristics of n-ZnO/p-GaN heterostructure.

shown in Fig. 4, the EL spectra of the forward biased LED consists of a broad emission band with a λ_{max} at about 430 nm and a FWHM of about 25 nm. The peak emission at 430 nm lies in the violet part of the spectrum, and there is a tail that extends to longer wavelengths. Our results are in agreement with the previous works that showed that 430 nm radiation is emitted whenever electrons are injected from the n region into a Mg-doped p region of GaN.[13,18,19] A comparison of Fig. 4 with the CL spectra of ZnO and GaN, shown in Figs. 2(a) and 2(b), suggests that the EL emission of our n-ZnO/p-GaN heterostructure emerges from the GaN side of the heterostructure. Thus, the EL properties of the formed n-ZnO/p-GaN heterostructure LED are determined primarily by electron injection from the n-ZnO side of the n-ZnO/p-GaN to the p-GaN side, where radiative recombination occurs. The likelihood of this scenario is increased when one considers that the donor concentration in ZnO:Ga is approximately one order of magnitude higher than the acceptor concentration in GaN:Mg (4.5×10^{18} cm^{-3} and 3.5×10^{17} cm^{-3}, respectively). As seen from the EL spectra in Fig. 4, there is no 383 nm peak as in the case of the GaN CL spectrum [Fig. 2(b)]. This can possibly be explained by self-absorption effects in the upper ZnO layer because the 383 nm emission wavelength of GaN is shorter than the 390 nm wavelength associated with excitonic emission of ZnO.[12]

The EL spectra of the n-ZnO/p-GaN heterostructure LED were measured at different injection currents. The measurements showed that the shape of the EL spectrum does not change significantly with the injection current, except that the FWHM exhibits a slight increase. Significantly, no shifting of the peak emission was observed within the injection current range employed in this work. The light–current ($L-I$) characteristics have been obtained from a direct measurement of the peak emission intensity at 430 nm, the results of which are shown in Fig. 5. In agreement with the spectral evolution, the $L-I$ curve shows a superlinear dependence at low currents (<10 mA) with a slope 1.9 ($L \sim I^m, m = 1.9$) which becomes sublinear ($m = 0.85$) at higher currents (>10 mA). We believe that the change in the slope corresponds to the current value at which the intensity of
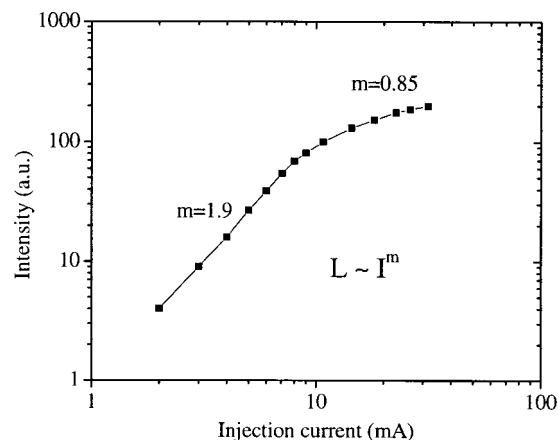
blue-violet emission at 430 nm is saturated. However, it can also be caused by Auger recombination at high injection current densities and by heating effects or series resistances, the quantification of which would require further investigation.

In conclusion, we have detailed the growth, processing, and fabrication of an n-ZnO/p-GaN(0001) heterojunction LED on an Al$_2$O$_3$(0001) substrate, and characterized the high-intensity electroluminescence from this device. Diode-like $I-V$ characteristics and RT EL in the blue-violet region has been observed under forward bias. $L-I$ characteristics of this structure were quantified, and behavior consistent with typical LEDs was revealed.

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