

## Fabrication and characterization of *n*-ZnO/*p*-AlGaN heterojunction light-emitting diodes on 6H-SiC substrates

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We report on the fabrication of *n*-ZnO/*p*-AlGaN heterojunction light-emitting diodes on 6H-SiC substrates. Hydride vapor phase epitaxy was used to grow *p*-type AlGaN, while chemical vapor deposition was used to produce the *n*-type ZnO layers. Diode-like, rectifying *I*-*V* characteristics, with threshold voltage  $\sim 3.2$  V and low reverse leakage current  $\sim 10^{-7}$  A, are observed at room temperature. Intense ultraviolet emission with a peak wavelength near 389 nm is observed when the diode is forward biased; this emission is found to be stable at temperatures up to 500 K and shown to originate from recombination within the ZnO. © 2003 American Institute of Physics.

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Zinc oxide, with a direct bandgap of  $\sim 3.3$  eV and an exciton binding energy of  $\sim 60$  meV, is a promising semiconductor for the fabrication of ultraviolet light-emitting diodes (LEDs) suitable for operation in harsh environments and at high temperatures.<sup>1</sup> ZnO has a number of advantages compared to those in other wide-band semiconductors (GaN, SiC), including higher quantum efficiency, greater resistance to high-energy radiation, and the possibility of wet chemical etching.<sup>1,2</sup> However, despite much progress in ZnO technology in recent years, high-quality *p*-type ZnO and therefore, the manufacture of ZnO homojunctions, continues to be problematic.<sup>2</sup> For now, the properties of ZnO might be best exploited by constructing heterojunctions with ZnO active regions; in this way, the emission properties of an LED can still be determined by the advantageous properties of ZnO. There are several reports<sup>3-5</sup> on the growth of *n*-type ZnO on *p*-type materials (ZnTe,<sup>3</sup> Cu<sub>2</sub>O,<sup>4</sup> and SrCu<sub>2</sub>O<sub>2</sub>)<sup>5</sup> to form LEDs with ZnO active regions; however, in all cases, the heterointerface has had to accommodate a large lattice mismatch that has greatly compromised device performance. Dislocations formed at the device interface as a result of strain relaxation generally form nonradiative defects that can seriously reduce the quantum efficiency of LEDs. The number of these nonradiative defects is itself a strong function of the buffer layer and substrate quality. In contrast, it was earlier shown that GaN makes an excellent buffer layer for ZnO, because the crystal structures are identical, and the lat-

tice constants are quite close.<sup>6</sup> In this work, we report on the fabrication of ZnO/AlGaN LEDs, taking advantage of the fact that AlGaN is also well matched to ZnO and can be doped *p*-type.<sup>7</sup>

GaN and AlN have bandgap energies of 3.4 and 6.2 eV, and lattice mismatches with ZnO of 1.8% and 4.4%, respectively;<sup>8</sup> in addition, many other physical properties are very close to those of ZnO.<sup>7,8</sup> For AlGaN alloys the lattice parameters are assumed to be linearly dependent on Al content and in our case, Al<sub>0.12</sub>Ga<sub>0.88</sub>N, the lattice mismatch is estimated to be 2.2%. Silicon carbide (6H-SiC) was used as a substrate, since it is known to be suitable for growing AlGaN, and is currently widely employed in the production of GaN-based devices.

A schematic diagram of our heterostructure is shown in Fig. 1. Commercial, *n*-type 6H-SiC wafers were used as substrates. First of all, epitaxial *n*-type GaN buffer layers of 0.2  $\mu\text{m}$  thickness were grown by hydride vapor phase epitaxy (HVPE). Next, Mg-doped, *p*-type AlGaN epitaxial layers of 0.8  $\mu\text{m}$  thickness and 12% Al content were grown, also by HVPE. Aluminum compositions in the AlGaN epilayers were estimated using x-ray diffraction (XRD), and the concentration of uncompensated acceptors, determined by Hg-probe measurements and analysis of capacitance-voltage characteristics of Cr Schottky barriers, was found to be about  $5 \times 10^{17} \text{ cm}^{-3}$ . A layer of *n*-type ZnO, about 1.0  $\mu\text{m}$  thick, was grown on the *p*-Al<sub>0.12</sub>Ga<sub>0.88</sub>N using chemical vapor deposition stimulated by an rf-discharge plasma.<sup>9,10</sup> The substrate temperature during growth was 400 °C, and the donor

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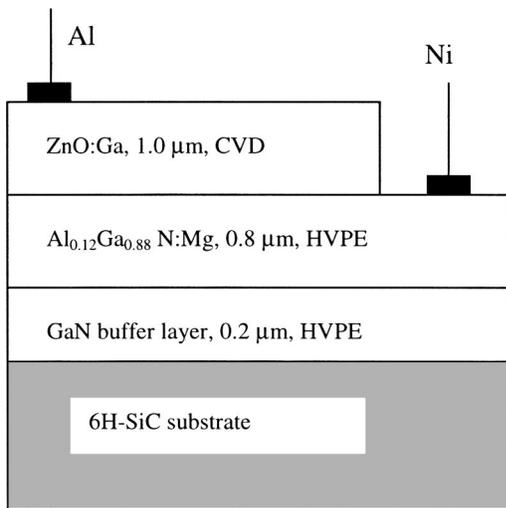


FIG. 1. Schematic diagram of the  $n$ -ZnO/ $p$ -Al<sub>0.12</sub>Ga<sub>0.88</sub>N heterojunction LED structure.

concentration, determined from Hall-effect measurements, was about  $7 \times 10^{17} \text{ cm}^{-3}$ . A Group III element, Ga, was used as the donor dopant since it is known to incorporate substitutionally on Zn lattice sites, forming a donor level with an activation energy of about 50 meV.<sup>10,11</sup>

Deposited films show high crystallinity, as evidenced by XRD and cathodoluminescence (CL) measurements. The heterojunction devices were fabricated by masking the surface, then using a 10% HNO<sub>3</sub> aqueous solution to etch down through  $2 \times 2 \text{ mm}^2$  windows to remove ZnO and leave regions of the AlGaN layer exposed. Ohmic contacts to the  $n$ -ZnO and  $p$ -Al<sub>0.12</sub>Ga<sub>0.88</sub>N were made by thermal vacuum deposition of Al and Ni, respectively. The optical properties of the ZnO and AlGaN films were explored using CL spectroscopy at room temperature, using an accelerating voltage of 20 keV and an electron-beam current of 0.1–1  $\mu\text{A}$ . Electroluminescence (EL) measurements were performed under dc-biased conditions at RT and 500 K.

The CL spectra of ZnO and Al<sub>0.12</sub>Ga<sub>0.88</sub>N films at RT are shown in Fig. 2. As seen from this figure, the CL spectrum of the ZnO film consists of intense, near-band-edge (NBE) UV emission with a wavelength maximum ( $\lambda_{\text{max}}$ ) at 387 nm and a full width at half-maximum (FWHM) of 21 nm. This ZnO CL NBE emission is of excitonic nature and is a result of the radiative annihilation of free and bound excitons.<sup>12,13</sup> A broad defect-related green band with much lower intensity

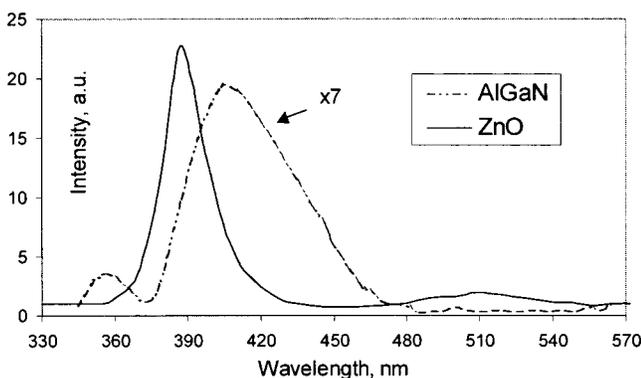


FIG. 2. RT CL spectra of ZnO and Al<sub>0.12</sub>Ga<sub>0.88</sub>N layers.

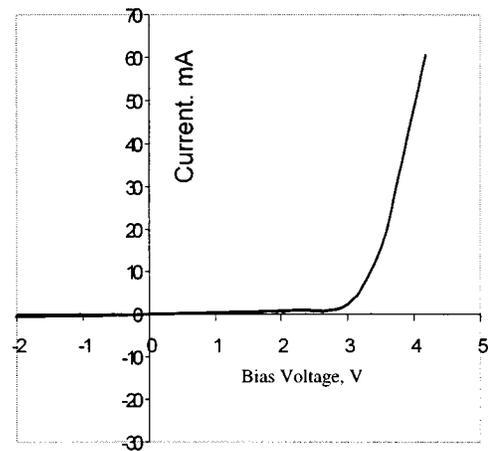


FIG. 3. RT  $I$ - $V$  characteristics of the  $n$ -ZnO/ $p$ -Al<sub>0.12</sub>Ga<sub>0.88</sub>N structure.

near  $\lambda_{\text{max}} \sim 510 \text{ nm}$  is also observed, as is typical in ZnO. The RT CL spectrum of the Al<sub>0.12</sub>Ga<sub>0.88</sub>N:Mg film is seen to consist of a very weak NBE band with  $\lambda_{\text{max}}$  at  $\sim 356 \text{ nm}$ , and of a more intense broad band with  $\lambda_{\text{max}} \sim 410 \text{ nm}$ .

The  $I$ - $V$  characteristics of the  $n$ -ZnO/ $p$ -AlGaN heterostructure at RT are presented in Fig. 3, and a rectifying diode-like behavior with threshold voltage  $\sim 3.2 \text{ V}$  is clearly observed. A high reverse breakdown voltage of almost 30 V and a small reverse leakage current of about  $10^{-7} \text{ A}$  are measured. The latter value is quite satisfactory, considering the large device contact area ( $2 \times 2 \text{ mm}^2$ ). At 4 V forward bias the injection current reaches 60 mA. The ideality factor  $n$ , calculated from the diode equation  $I = I_s [\exp(qU/nkT) - 1]$ ,<sup>14</sup> where  $I_s$  is the saturation current, is found to be approximately  $n = 3$ . From these data it can be seen that the  $I$ - $V$  characteristics of our structure are comparable to those of many other high-quality, wide-bandgap homojunction and heterojunction devices (see Refs. 15–17). It is interesting to note that these  $I$ - $V$  characteristics are much better than those observed in our previous work,<sup>18</sup> in which  $n$ -ZnO/ $p$ -GaN type heterostructures were grown onto poorly lattice-matched sapphire substrates. This fact further demonstrates the improvements brought about by the improved lattice matching in the  $n$ -ZnO/ $p$ -AlGaN/SiC structure.

As shown in Fig. 4, under forward bias the device produces intense UV EL with a peak emission near 389 nm

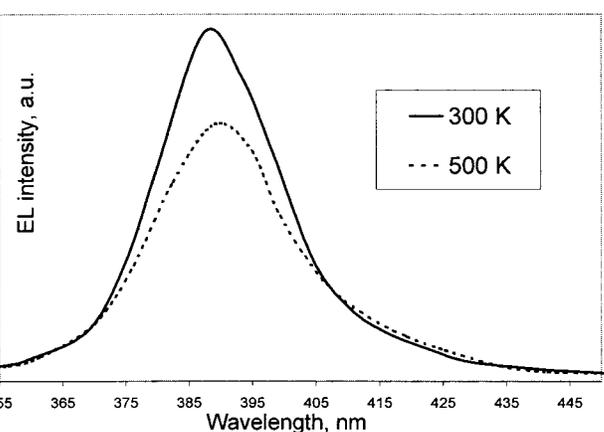


FIG. 4. EL spectra of an  $n$ -ZnO/ $p$ -Al<sub>0.12</sub>Ga<sub>0.88</sub>N heterostructure LED at 300 and 500 K ( $I_c = 20 \text{ mA}$ ).

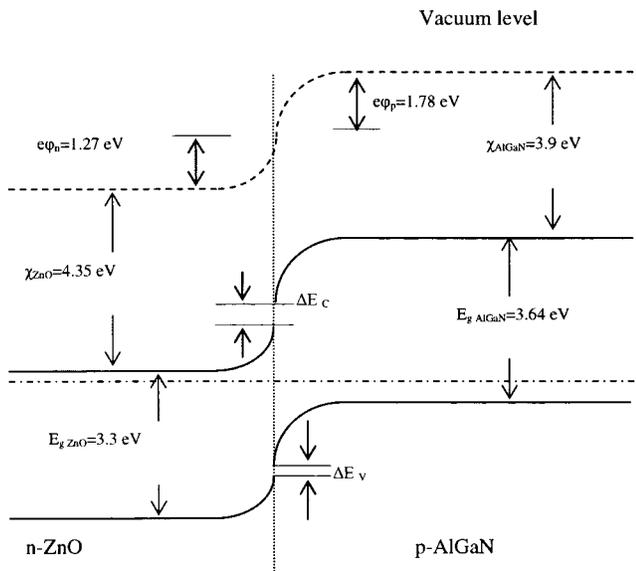


FIG. 5. Anderson model energy band diagram of  $n\text{-ZnO}/p\text{-Al}_{0.12}\text{Ga}_{0.88}\text{N}$  heterojunction.

(3.19 eV) and a FWHM of 26 nm. Significantly, no other emission bands are observed in the EL spectrum. By comparing the EL spectrum of our LED with the CL spectra of the individual heterostructure layers it can be concluded that the EL emission emerges from the ZnO region of the device, and the predominant device current is hole injection from the  $p$ -type  $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$  into the  $n$ -type ZnO region of the heterojunction. This conclusion is supported by the  $I$ - $V$  characteristics that show a threshold voltage of about 3.2 V, very close to the RT bandgap energy of ZnO ( $\sim 3.3$  eV). This is a likely outcome since energy band diagrams built using the Anderson model<sup>19</sup> show a much smaller barrier for holes than that which exists for electrons. This energy band diagram of  $n\text{-ZnO}/p\text{-Al}_{0.12}\text{Ga}_{0.88}\text{N}$  is presented in Fig. 5. In this diagram, the electron affinity for ZnO  $\chi_{\text{ZnO}}$  is taken as 4.35 eV,<sup>20</sup> and the electron affinity of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is assumed to be linearly dependent on  $x$  and to lie between 0.6 eV for AlN and 4.2 eV for GaN,<sup>21,22</sup> giving 3.9 eV for  $x=0.12$ . The bandgap energy of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  is also assumed to linearly depend on  $x$  and to lie in the range between 3.4 eV (GaN) and 6.2 eV (AlN),<sup>23</sup> leading to 3.64 eV for  $x=0.12$ . As can be seen from the diagram, the energetic barrier  $\Delta E_C$  for electrons is  $\Delta E_C = \chi_{\text{ZnO}} - \chi_{\text{AlGaIn}} = (4.35 - 3.9)$  eV = 0.45 eV, while the energetic barrier  $\Delta E_V$  for holes is  $\Delta E_V = E_{g,\text{ZnO}} + \Delta E_C - E_{g,\text{AlGaIn}} = (3.3 + 0.45 - 3.64)$  eV = 0.11 eV. Thus, the energetic barrier for holes  $\Delta E_V$  is over four times less than the barrier for electrons  $\Delta E_C$ .

The temperature dependence of the EL spectra was measured, and significant EL emission at temperatures up to 500 K was observed (see Fig. 4, dashed line). The EL intensity is seen to remain relatively high, while a slight redshift in peak wavelength (to about 391 nm) and some broadening (to 29 nm) is observed. The similarity of the ZnO-layer CL spectrum and the LED EL spectrum, and the thermostability of the emission and very large exciton binding energy of ZnO

( $\sim 60$  meV), suggest that the UV emission of the  $n\text{-ZnO}/p\text{-AlGaIn}$  LED is mainly excitonic in nature. In earlier reports, Bagnall *et al.*<sup>13</sup> observed stimulated excitonic emission at relatively high temperatures, up to 550 K. However, other radiative mechanisms, such as donor-acceptor, donor-hole, and acceptor-electron transitions can also take place and contribute to this EL NBE emission.

The dependence of EL spectra on injection current was also measured (not shown). With an increase in injection current, the EL intensity  $L$  grows superlinearly with low forward current  $I_c$  ( $L \sim I_c^{2.2}$ ), and the emission wavelength shifts slightly toward longer wavelengths, due to thermal effects.

In conclusion, we have fabricated bright UV LEDs based on ZnO active layers by using  $p$ -type AlGaIn to form a heterojunction. The stability of device performance at high temperature indicates possible applications in harsh environments. With further development, it may even be possible to fabricate UV laser diodes, with low, "excitonic" thresholds and high-temperature capability, by exploiting the thermal stability of the ZnO exciton.

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