Electroluminescence at 375 nm from a ZnO/GaN:Mg/*c*-Al_2O_3 heterojunction light emitting diode

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n-ZnO/*p*-GaN:Mg heterojunction light emitting diode (LED) mesas were fabricated on *c*-Al_2O_3 substrates using pulsed laser deposition for the ZnO and metal organic chemical vapor deposition for the GaN:Mg. High crystal quality and good surface morphology were confirmed by x-ray diffraction and scanning electron microscopy. Room temperature (RT) photoluminescence (PL) showed an intense main peak at 375 nm and a negligibly low green emission indicative of a near band edge excitonic emission from a ZnO layer with low dislocation/defect density. The LEDs showed *I-V* characteristics confirming a rectifying diode behavior and a RT electroluminescence (EL) peaked at about 375 nm. A good correlation between the wavelength maxima for the EL and PL suggests that recombination occurs in the ZnO layer and that it may be excitonic in origin. This also indicates that there is significant hole injection from the GaN:Mg into the ZnO. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2195009]

Efficient short-wavelength light emitters are necessary for emerging applications such as solid-state lighting and high density data storage.[1,2] At present, GaN (band gap energy E_g=3.39 eV) is the only wide band gap material which has been developed on an industrial scale for use in ultraviolet (UV) light emitting diodes (LEDs) and laser diodes (LDs).

ZnO (E_g=3.37 eV) is considered a promising material for the next generation of UV LED and LDs because it has a much larger exciton binding energy than GaN (~60 meV as opposed to 21 meV) which could lead to UV sources with higher brightness, lower threshold currents, better performance at high temperature, and a very high radiation resistance.[2–4] For the moment, however, reproducible and stable *p*-type ZnO material with sufficiently high conductivity and carrier concentration is still in a development phase, and homostructural ZnO LEDs and LDs are not readily available.[3]

In an alternative approach, there have been numerous attempts to develop *p-n* heterojunction LEDs with ZnO as the *n*-type layer.[15,16] It is hoped that such hybrid devices could also benefit from robust excitonic emission if the radiative recombination occurs in the ZnO layer.[9,16] These attempts have employed a wide range of *p*-type materials and a large variety of thin film growth tools. To date, however, there have been few publications reporting electroluminescence[5–14,16] (EL) in such heterostructures, and only three have exhibited a dominant UV emission which has been attributed to radiative recombination in the ZnO (at 382,[7] 389,[9] and 390 nm[16]). High quality epitaxy and a good interface at the *p-n* junction are cited as key factors in the quest to improve such devices, because defects/dislocations and/or impurities act as nonradiative recombination centers. Lattice mismatch between the substrate, ZnO, and the *p*-type underlayer is an important factor determining the quality of the epitaxy and the density of defects/dislocations in the heterostructure. GaN based films are considered good candidates for the *p*-type layer because they are readily available and they have the same crystal structure (wurtzite) as ZnO with a small in-plane lattice mismatch (~1.8% for GaN) and the same stacking sequence (2H).[17]

Recently, Alivov *et al.*[8,9] compared growth of *n*-ZnO:Ga (by chemical vapor deposition) on both *p*-GaN:Mg/*c*-Al_2O_3 and *p*-$Al_{0.12}Ga_{0.88}N$:Mg/6*H*-SiC. Both types of heterojunction showed a RT EL. The ZnO/GaN had a wavelength maximum (λ_{max}) at 430 nm while the ZnO/AlGaN had a λ_{max} at 389 nm. From correlations with cathodoluminesence spectra it was inferred that the former was due to radiative recombination in the GaN while the latter was due to radiative recombination in the ZnO. The ZnO/AlGaN heterojunction showed a much better *I-V* characteristic and optical power output than the ZnO/GaN.

These differences were attributed to two main factors: (1) band lineup calculations based on the Thomson model[9,18] suggesting that electron injection from the *n*-ZnO into the *p*-GaN should be more energetically favorable than hole injection from the *p*-GaN into *n*-ZnO while hole injection from *p*-$Al_{0.12}Ga_{0.88}N$ into *n*-ZnO would be more favorable than electron injection from *n*-ZnO into *p*-$Al_{0.12}Ga_{0.88}N$ and (2) improved epitaxy and reduced defect/dislocation density in the ZnO/AlGaN due to the use of a 6*H*-SiC substrate (a *c*-Al_2O_3 substrate was employed for the ZnO/GaN). 6*H*-SiC has a lower lattice mismatch with GaN than *c*-Al_2O_3 (~5% as opposed to ~16% for the *c*-Al_2O_3).[17]

In spite of these findings, it was decided to pursue the growth of *n*-ZnO on *p*-GaN buffered Al_2O_3, but using a different approach. The reasoning for this was fourfold. Firstly, calculations based on the Thomson model give an idea of the band lineup in an idealized system but they do not definitively preclude hole injection into *n*-ZnO from *p*-GaN

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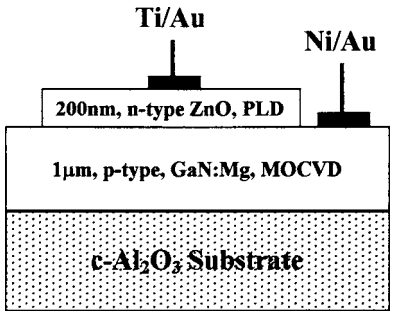

FIG. 1. Cross-sectional schematic of the *n*-ZnO/*p*-GaN:Mg heterojunction LED mesa structure.

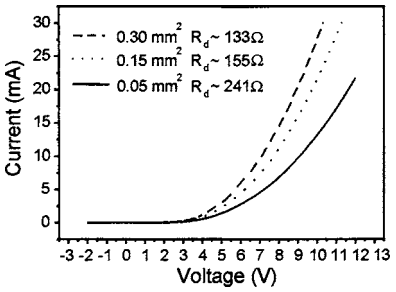

FIG. 3. RT *I-V* characteristics for the *n*-ZnO/*p*-GaN:Mg mesa structures. Differential resistance (R_d) for each mesa area is also indicated on the graph.

because the ZnO/GaN/*c*-Al_2O_3 is far from an ideal system in that it is lattice mismatched, involves strongly polar materials, and probably presents significant imperfections at the heterojunction interface. Secondly, the adoption of pulsed laser deposition (PLD) for the ZnO growth could give higher quality epitaxy of ZnO on such highly lattice-mismatched substrates.[19] Thirdly, *c*-Al_2O_3 substrates are much cheaper than 6*H*-SiC substrates. Finally, *c*-Al_2O_3 substrates are transparent, which offers the advantage of much better light extraction potential than opaque 6*H*-SiC substrates.

In our experiment (Fig. 1) a 1 μm thick Mg doped GaN layer (GaN:Mg) was grown on *c*-Al_2O_3 by metal-organic chemical vapor deposition (MOCVD) using a low-pressure horizontal-flow reactor. Trimethylgallium, NH_3, and bis(cyclopentadienyl)magnesium were used as the sources for Ga, N, and Mg, respectively, as described elsewhere.[20] After rapid thermal annealing in N_2 at 1000 °C Hall measurements reveal a *p*-type behavior for the GaN with a carrier concentration of about 5×10^{17} cm^{-3} and a resistivity of about 0.8 Ω cm.

A ZnO layer was grown on top of the GaN:Mg layer using PLD in a molecular oxygen ambient with a KrF excimer laser (248 nm), as described elsewhere.[21] Such nominally undoped ZnO exhibits *n*-type behavior with a carrier concentration of about 2×10^{17} cm^{-3} [the nature of the dominant donor(s) remains controversial but it is thought that it may be Al and/or Ga].[2,22] x-ray diffraction (XRD) studies of the ZnO/GaN/Al_2O_3 heterostructures showed that the GaN and ZnO were both of high crystal quality with (0002) omega-scan full width at half maximum (FWHM) of 340 and 430 arc sec, respectively. ZnO growth was seen to result in the appearance of Kiessing fringes, in the two theta-omega scan, indicative of low surface roughness. A smooth film surface, free of ablated particulates, was confirmed using scanning electron microscopy (SEM).

The optical properties of the ZnO and GaN films were investigated using RT photoluminescence (PL) spectroscopy with an Ar ion laser (Fig. 2). Prior to growth of the ZnO, the GaN:Mg layer exhibited strong PL with weak near band edge (NBE) emission at about 365 nm and a dominant deep acceptor peak with a λ_{max} at around 408 nm and a FWHM of about 40 nm. This is typical for Mg doped GaN and is generally attributed to transitions from the conduction band, or shallow donors, to deep Mg levels.[23,24]

In the PL spectrum for the ZnO/GaN:Mg heterostructure the emission peaks for the GaN:Mg underlayer are no longer present, possibly due to self-absorption in the ZnO layer. A new peak has appeared, however, with a λ_{max} of about 375 nm, a FWHM of about 25 nm, and a significantly higher intensity than the emission from the GaN:Mg underlayer (N.B. the intensity scale for the ZnO and GaN spectra in Fig. 2 is not the same). This λ_{max} (at 3.31 eV) is characteristic of NBE emission from ZnO. Such short-wavelength NBE emission has only been observed in high quality ZnO layers and has been associated with radiative recombination of free and bound excitons.[4] The broadening on the longer-wavelength side of the main peak can be attributed to phonon replicas due to strong exciton coupling with longitudinal optical phonons. The absence of the (deep level) green band luminescence generally observed in the PL spectrum for a ZnO layer suggests that the ZnO has relatively few defects/dislocations (the intensity at 500 nm is more than 40 000 times lower than the NBE emission). Circular LED mesas were fabricated from the heterostructure by masking the surface and chemically etching away the ZnO layer. Six different mesa size, gave areas ranging from 0.05 up to 0.30 mm^2 in increments of 0.05 mm^2. Semitransparent Ni/Au contacts were evaporated onto the *p*-type GaN:Mg and Ti/Au contacts were evaporated onto the *n*-type ZnO.

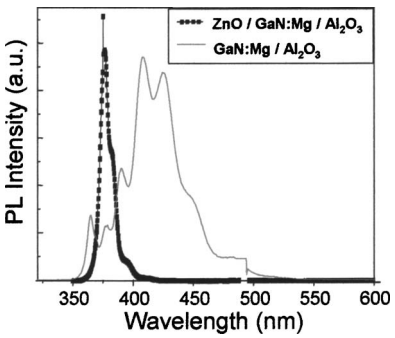

FIG. 2. Room temperature photoluminescence spectra from the ZnO/GaN:Mg heterostructure before and after the growth of ZnO (N.B. the artifact at 488 nm is due to filtering employed to block the second harmonic of the laser).

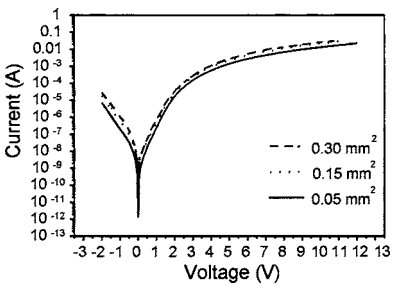

FIG. 4. RT log (*I-V*) characteristics for the *n*-ZnO/*p*-GaN:Mg mesa structures.

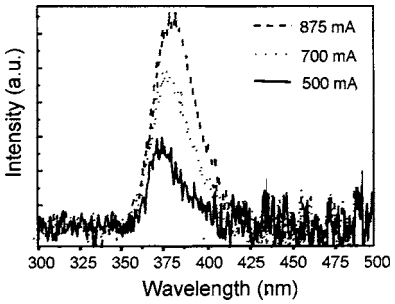

FIG. 5. EL spectra for *n*-ZnO/*p*-GaN:Mg heterostructure LED at RT for various forward drive currents.

RT *I-V* characteristics of various LED mesas are shown in Figs. 3 and 4. All curves exhibit nonlinear rectifying behavior with a forward bias switch-on voltage of about 3.3 V, which corresponds to the E_g for ZnO. The turn-on is gradual and follows a I-V^2 relationship over a wide range of forward bias, as might be expected for such a wide band gap material.[25,26] We observe a leakage current of about 14 mA/cm^2 at $V=-2$ V and a reverse bias breakdown voltage of about 6 V at RT.

Figure 5 shows the EL emission from the *n*-ZnO/*p*-GaN:Mg heterostructure under forward bias (in pulsed injection mode: duty cycle of 1%) at RT. The spectrum consists of a single peak with a λ_{max} at 375 nm and a FWHM of about 25 nm. This λ_{max} is the same as that observed in the PL spectrum, which suggests that the radiative recombination occurs in the ZnO layer and, hence, that the EL emission may be excitonic in nature. As the injection current is increased from 500 to 875 mA, λ_{max} is slightly redshifted to ~381 nm (probably due to thermal effects) and the peak broadens a little to a FWHM of about 31 nm. Over the injection current range from 500 to 875 mA the light-current (*L-I*) characteristic of spectral intensity versus current appears fairly linear. This suggests that, even at 875 mA, we have not saturated the UV emission.

Figure 6 shows the EL light power as a function of forward bias current, in pulsed injection mode. Light was collected using a calibrated integrating sphere positioned with input port almost flush with the topside of the device. These curves show that LEDs ranging from 0.05 up to 0.3 mm^2 in size have similar outputs, which indicates that there is a good lateral homogeneity of the layer/device properties. The light conversion efficiency is about 0.000 05%.

In conclusion, we fabricated a *n*-ZnO/*p*-GaN:Mg heterostructure on a *c*-Al_2O_3 substrate. XRD, SEM, and PL indicate that we achieved high quality epitaxy with low defect/dislocation density on *c*-Al_2O_3 substrates by combining MOCVD and PLD. The heterojunction exhibited RT EL at 375 nm. The correlation between the λ_{max} for the heterojunction EL and the RT PL peak associated with the ZnO layer suggests that recombination occurs in the ZnO layer, and that it may be excitonic in origin. This, in turn, indicates that it is possible to obtain significant hole injection from the GaN:Mg into intrinsically doped ZnO. *I-V* characteristics confirm a rectifying diode behavior. These results show that *n*-ZnO/*p*-GaN:Mg/*c*-Al_2O_3 heterostructures have potential for use as UV LEDs which benefit from the robust excitonic emission from ZnO. Compared with 6*H*-SiC substrates, the use of transparent *c*-Al_2O_3 substrates adds the advantages of better light extraction potential and lower cost.

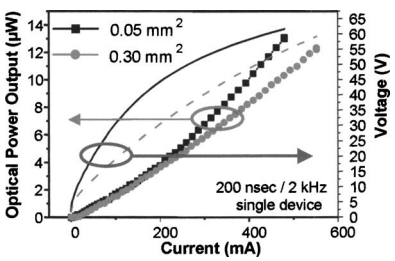

FIG. 6. Optical power output and operating voltage as functions of forward drive current for the largest and smallest of the *n*-ZnO/*p*-GaN:Mg heterojunction LED mesas.

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