Observation of 394 nm electroluminescence from low-temperature sputtered *n*-ZnO/SiO_2 thin films on top of the *p*-GaN heterostructure

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The authors report on the 394 nm UV light emission from low-temperature sputtered *n*-ZnO/SiO_2 thin films on top of the *p*-GaN heterostructure. They compare samples with and without a SiO_2 current blocking layer. With a SiO_2 layer, electroluminescence spectrum shows a sharp emission peak at 394 nm, which is attributed to the recombination of accumulated carriers between *n*-ZnO/SiO_2 and *p*-GaN/SiO_2 junctions. As for the sample without a SiO_2 layer, a broadband ranging from 400 to 800 nm is observed, which is due to Mg^+ deep-level transition in the GaN along with defects in the ZnO layers. © *2007 American Institute of Physics*.
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ZnO, with a large direct band gap of 3.37 eV, is a promising material for ultraviolet (UV) light emissions or photodetections. It possesses unique characteristics such as a large exciton binding energy of 60 meV (versus 26 meV for GaN), easy processing due to amenability to conventional chemical wet etching, and the possibility of low-temperature growth. Up to the present, heterostructure light emitting diodes (LEDs) have been demonstrated by growing *n*-type ZnO on top of a variety of *p*-type layers such as GaN, Si, $SrCu_2O_2$, etc.[1–4] Moreover, even though the development of high-quality *p*-type epitaxial growth for *p*-type ZnO is relatively slow, *p-n* ZnO diodes have also been realized.[5]

Several different emission wavelengths of ZnO heterostructure LEDs have been presented, ranging from UV emission at 375–389 nm to wideband spectra (violet-white to blue-white).[6] For example, Alivov *et al.* compared growth of *n*-ZnO:Ga by chemical vapor deposition (CVD) on both *p*-GaN:Mg/*c*-Al_2O_3 and *p*-$Al_{0.12}Ga_{0.88}N$:Mg/6*H*-SiC structures.[1,7] The wavelength maximum is 430 nm for ZnO/GaN LEDs and 389 nm for ZnO/AlGaN devices. It was inferred 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*-AlGaN into *n*-ZnO will be more favorable than electron injection from *n*-ZnO into *p*-AlGaN.[8] Furthermore, Jiao *et al.*[9] fabricated *n*-ZnO/*p*-GaN diodes with a MgO layer for electron blocking. The result showed a peak wavelength at 380 nm.

Despite excellent results of UV light emission from previous studies of ZnO/GaN based heterostructures, most recent studies have focused on carrier recombinations in the ZnO layer. Therefore, in addition to efficient current blocking structures, various growth methods were employed to achieve quality ZnO epitaxy for sharp excitonic emission peaks.[6] In this work, we demonstrate a 394 nm UV electroluminescence (EL) light emission from a *n*-ZnO/SiO_2/*p*-GaN heterostructure. Photoluminescence (PL), current-voltage diode curves, and EL measurement were conducted to characterize ZnO/GaN LEDs with and without a SiO_2 current blocking layer.

The fabrication started from the preparation of a *p*-type GaN epiwafer. The *p*-type GaN layer was grown on top of a sapphire substrate by metal-organic CVD (MOCVD). The effective carrier concentration in this layer is approximately 5×10^{17} cm^{-3} after *p*-GaN activation. In the next step, a 300×300 μm^2 patterned SiO_2 layer was coated on top of the *p*-GaN layer at room temperature, followed by the deposition of a 300 nm heavily doped *n*-type ZnO at 100 °C, both by rf magnetron sputtering. The 3 nm SiO_2 layer is inserted between *p*- and *n*-type layers for carrier blocking. We also prepared a LED sample without a SiO_2 layer for comparison. The sputter target of the *n*-type ZnO was doped with 0.5 wt % Ga, and the ZnO layer was annealed at 550 °C for 30 min after deposition. Finally, Ni/Au and Ti/Au were evaporated as the *p*-type and *n*-type contact electrodes, respectively. They were alloyed for optimum contact conditions.

We first perform room temperature PL measurement on a sputtered *n*-ZnO thin film as well as a *p*-GaN sample by a He–Cd laser operating at 325 nm. As shown in Fig. 1, the PL spectrum of the *n*-ZnO shows a near-band-edge (NBE) emission at 379 nm and a wide green band at 503 nm. Green luminescence has been reported to be due to oxygen vacancy related defects in the crystallite surface.[10] Despite the fact that the intensity ratio between defect related and NBE emission is higher than other approaches such as pulsed laser deposition or CVD due to the low-temperature sputtering

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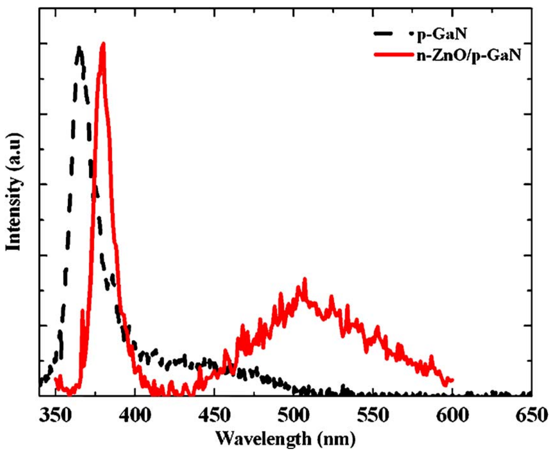

FIG. 1. PL spectra of rf sputtered *n*-ZnO (solid line) and MOCVD grown *p*-GaN (dashed line).

process, the sharp excitonic peak at 379 nm suggests that the material property is suitable for light emitting devices. In contrast, the PL spectrum of the *p*-GaN film reveals an intense deep-level emission at around 430 nm, which can be attributed to the transmission from the conduction band or shallow donors to the Mg acceptor doping level.[11]

Figure 2 shows the *I-V* curves of heterojunction devices with and without a SiO_2 current blocking layer. Both samples demonstrate a nonlinear rectifying behavior while an additional voltage drop across the SiO_2 layer is observed from the *n*-ZnO/SiO_2/*p*-GaN device. The large threshold voltage of both samples is related to the Schottky barrier between the contact electrode and the ZnO layer. EL spectra of these two devices are shown in Figs. 3(a) and 3(b), respectively. For the LED without a current blocking layer, a wideband emission between 400 and 800 nm can be seen. By comparing the EL curves in Fig. 3(a) with PL spectra in Fig. 1, the emission peaks between 421 and 438 nm result from deep-level carrier recombination in the *p*-GaN layer, while long tails are due to oxygen vacancies in the *n*-ZnO layer. As the injection current is increased, a blueshift is noted which is related to band filling in the *p*-GaN layer.[12] As for the EL spectra of the sample with a SiO_2 layer, the emission maximum starts from 421 nm at a low injection current 5 mA, which, by comparing with the spectra in Figs. 1 and 3(a), indicates that recombination occurs in the *p*-GaN layer. When we further

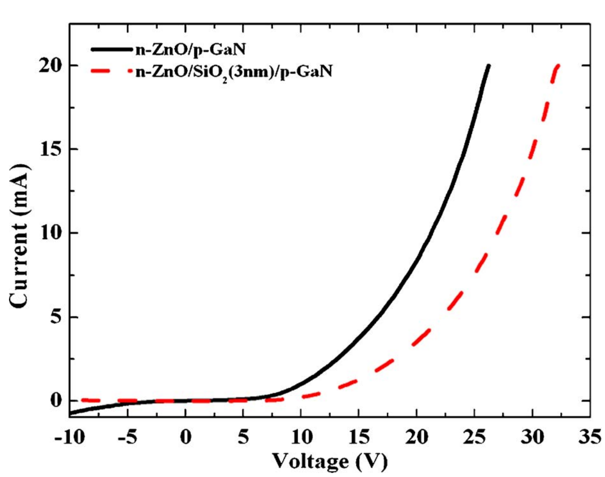

FIG. 2. *I-V* curves of a *n*-ZnO/*p*-GaN LED (solid line) and a *n*-ZnO/SiO_2 (3 nm)/*p*-GaN LED (dashed line).

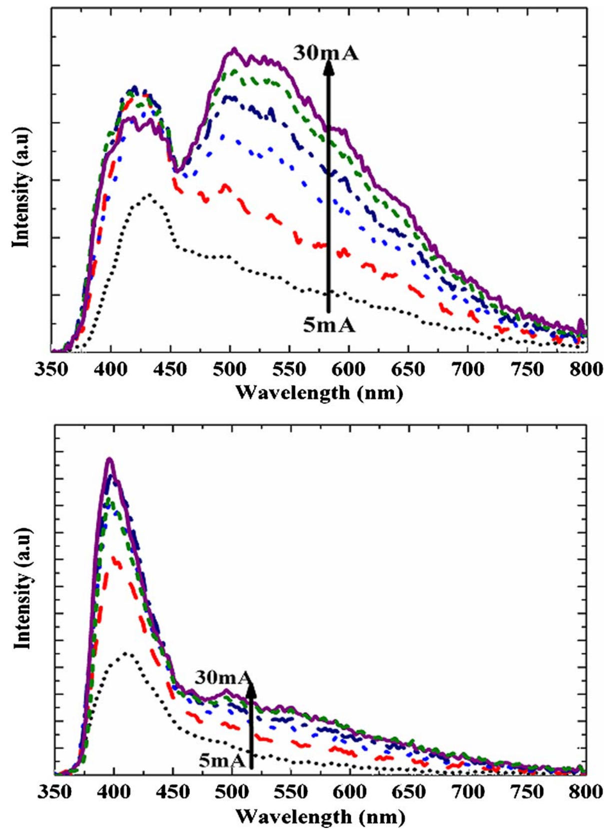

FIG. 3. EL spectra of a ZnO–GaN LED (a) and a *n*-ZnO/SiO_2 (3 nm)/*p*-GaN LED (b). The bias current ranges from 5 to 30 mA at a step 5 mA.

raise the bias voltage to a point that enough electrons and holes accumulate in the interface of *n*-ZnO/SiO_2 and *p*-GaN/SiO_2, respectively, recombination between *n*-ZnO and *p*-GaN by carriers through the SiO_2 can be found from the EL peak at 394 nm. Therefore, the emission peak shifts from 421 nm at 5 mA to 394 nm at injection currents above 10 mA. No significant wavelength shift can be observed for currents beyond 10 mA.

The emission at an optical energy lower than the NBE of ZnO can be described from the band diagram constructed from Anderson model. In Fig. 4, the energy barrier for ΔE_C and ΔE_V in the interface of ZnO/SiO_2 and GaN/SiO_2, determined from electron affinity and band gap, is 3.24 and 2.5 eV, respectively. Therefore, the EL emission peak is shifted toward a longer wavelength due to the band offset at

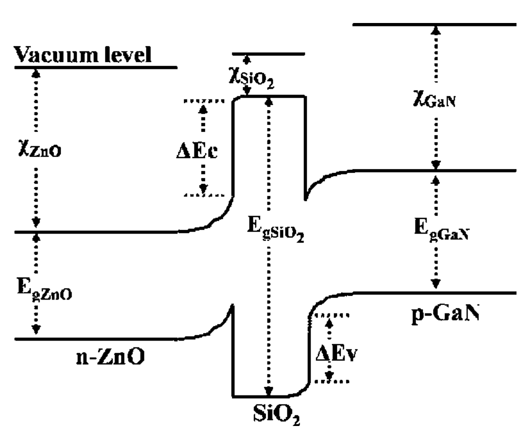

FIG. 4. Band gap diagram of the *n*-ZnO/SiO_2/*p*-GaN structure.

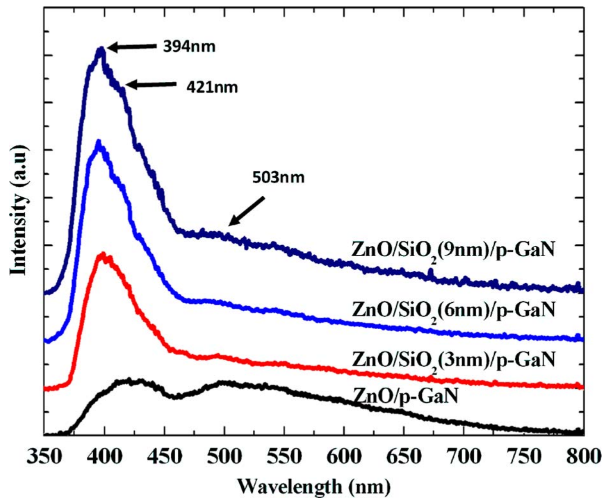

FIG. 5. EL spectra of n-ZnO/SiO_2/p-GaN LEDs with different SiO_2 thicknesses. The bias current is 20 mA. The EL intensity is expressed in linear scale.

the valence of p-GaN. The result implies that with the insertion of a current blocking layer, the emission wavelength can be controlled by selecting different band gap structures of both the n-type and p-type layers.

We further extend the thickness of SiO_2 layers to 6 and 9 nm. Figure 5 demonstrates the EL spectra of samples with 0, 3, 6, and 9 nm thickness of SiO_2 layers biased at an injection current of 20 mA. All the samples have the same layout structure and p-type mesa area of $300 \times 300\ \mu m^2$. It is shown that the emission maximum occurs at 394 nm for the sample with a blocking layer and at 421 nm for the n-ZnO/p-GaN sample. Also, we have noticed that the relative intensity of the n-ZnO/p-GaN sample is much weaker than that of samples with the SiO_2 layer. The quantum efficiency, calculated from the EL spectra at 20 mA, of sample with 3, 6, and 9 nm SiO_2 is 7.6%, 24.5%, and 57.2%, respectively, higher than that of a n-ZnO/p-GaN device. It indicates that the SiO_2 layer helps confine carriers for the recombination between junctions of n-ZnO/SiO_2 and SiO_2/p-GaN, and, thus, less carriers are consumed in the n-ZnO or p-GaN layer despite subpeaks at 421 and 503 nm can still be observed for devices with SiO_2. By comparing the EL spectra of the device without SiO_2, those humps are related to carrier recombination in the n-ZnO and p-GaN layers. In this experiment, we also fabricated a sample with 12 nm SiO_2 layer. But unfortunately the required bias voltage is too large to be of practical measurement.

In conclusion, we fabricated a n-ZnO/SiO_2/p-GaN light emitting diode with 394 nm UV light emission. We compare samples with and without a SiO_2 current blocking layer. With a SiO_2 layer, EL spectrum shows a sharp emission peak at 394 nm. The 394 nm peak is attributed to the recombination of accumulated carriers between n-ZnO/SiO_2 and p-GaN/SiO_2 junctions. As for the sample without a SiO_2 layer, only the 400–800 nm broadband is observed, which is due to Mg^+ deep-level transition in the GaN and defects related recombination in the ZnO layers

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