UV Electroluminescence Emission from ZnO Light-Emitting Diodes Grown by High-Temperature Radiofrequency Sputtering

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UV light-emitting devices (LEDs) and laser diodes (LDs) are of interest for their potential use in long-lifetime solid-state lighting, high-density information storage, secure communication, and chemical/biological agent monitoring.[1] Recently, intensive research efforts have been focused on finding materials to realize efficient UV LEDs and LDs.[2] Among the available wide-bandgap semiconductors, zinc oxide, with a large direct bandgap of 3.37 eV, is a promising candidate for use as an efficient UV-light emitter because of characteristic features such as a large exciton binding energy of 60 meV, and the realization of bandgap engineering to create barrier layers and quantum wells with little lattice mismatch.[3] The commercial availability of large-area ZnO substrates and the possibility of performing wet etching also make the fabrication of ZnO-based optical devices an attractive prospect, as it would enable the fabrication of vertical-geometry devices with low threading dislocation densities by a simple process.[4] However, p-type ZnO does not exist naturally and considerable efforts have been made to produce it by impurity doping.[5]

Difficulties in obtaining p-type ZnO has recently led to the fabrication of p–n heterojunction LEDs by growing n-type ZnO on other p-type materials such as p-SrCu2O2, p-GaN, and p-AlGaN.[6] A few studies have also been reported on the rectifying current–voltage (I–V) characteristics and the electroluminescence (EL) of p–n homojunction ZnO LEDs at room temperature.[7] However, the EL emission peaks obtained from these homojunction LEDs did not show the near-bandedge emission of ZnO at about 380 nm. The failure to observe the near-bandedge emission was increased and the deep-level emission was decreased when (Mg,Zn)O alloy layers were introduced as energy barrier layers between n-type and p-type ZnO films to confine the carrier recombination process to the high-quality n-type ZnO film.

A schematic diagram of the p–n homojunction ZnO LED is shown in Figure 1. The gallium-doped n-type ZnO with a thickness of 1.5 µm was grown on a c-Al2O3 substrate. It to improve the structural properties of n- and p-type ZnO compared to previous studies.[7] In addition, a thermal annealing process was carried out to activate the phosphorus dopants in p-type ZnO and improve the electrical and optical properties of the ZnO layers. The LED showed excellent current-rectifying behavior with a threshold voltage of 3.2 V and an EL emission peak at 380 nm at room temperature. The UV EL emission spectrum was in good agreement with the room-temperature photoluminescence (PL) spectrum of the p-type ZnO used in the LED. Furthermore, the near-bandedge emission was increased and the deep-level emission was decreased when (Mg,Zn)O alloy layers were introduced as energy barrier layers between n-type and p-type ZnO films to confine the carrier recombination process to the high-quality n-type ZnO film.

Figure 1. A) Schematic diagram of a p–n homojunction ZnO LED. B) Cross-sectional transmission electron microscopy (TEM) image of the region around the p-type ZnO (top)/n-type ZnO (bottom) interface with the electron beam along the [270]ZnO direction. The inset shows the corresponding electron diffraction pattern.

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showed a carrier concentration of $2.2 \times 10^{18} \text{ cm}^{-3}$ and a mobility of 40 cm$^2$ V$^{-1}$ s$^{-1}$. Gallium was used as the n-type dopant since it is less susceptible to oxidation than other group III elements and causes less deformation of the ZnO lattice even at high doping concentrations.$^8$ The phosphorus-doped p-type ZnO layer with a thickness of 0.4 μm was grown on the n-type ZnO film. The hole concentration and the mobility of the p-type ZnO were $1.0 \times 10^{19} \text{ cm}^{-3}$ and 1 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, after a rapid thermal annealing process in a N$_2$ atmosphere at 800 °C for 5 min.$^9$ Figure 1B shows a high-resolution transmission electron microscopy (HRTEM) image of the p–n junction region of the LED, with the electron beam along the [2110]$_{ZnO}$ direction. The image shows that the p-type ZnO was epitaxially grown on the n-type ZnO layer without the formation of any interfacial phase. However, some stacking faults were observed in the p-type ZnO layer, as indicated by the arrows in Figure 1B. This result shows that the p-type ZnO film is highly c-axis oriented and has a low density of defect centers responsible for the nonradiative recombination. In addition, the electron diffraction pattern of the same region shown in the inset of Figure 1B suggests that the crystallographic alignment of the n- and p-type ZnO layers at the interface is excellent, resulting in good matching of symmetry and lattice spacing.

The $I$–$V$ characteristics of the homojunction ZnO LED are shown in Figure 2. The device shows clear rectification with a threshold voltage of 3.2 V, which is in good agreement with the ZnO bandgap energy of 3.37 eV. The NiO/Au contact to the p-type ZnO layer and the Ti/Au contact to the n-type ZnO layer showed good ohmic behavior, as shown in the inset of Figure 2A, confirming that the rectification in Figure 2A arises from the p–n junction. The rectification ratio of the forward to reverse bias current was approximately 1000:1 at a bias voltage of ±3.5 V, as shown in Figure 2B. This value indicates that the LED has a low defect density and a low tunneling current. The diode ideality factor was determined to be 2.5 at a low bias voltage, indicating that electron–hole recombination occurs over a wide region of the p–n junction.$^{10}$

The room-temperature PL spectra of separately grown n-type and p-type ZnO films are shown in Figure 3A. The PL spectrum of n-type ZnO on c-Al$_2$O$_3$ showed an intense near-bandedge emission peak at 380 nm with a full width at half maximum (FWHM) of 19 nm. This peak is slightly red-shifted from the ZnO bandedge emission of around 360 nm$^{11}$ because of an emissive transition from an impurity donor band to a valence band.$^{12}$ The PL spectrum of a p-type ZnO film grown on an undoped, 1 μm thick ZnO buffer layer also showed a strong near-bandedge emission peak at 380 nm at room temperature as shown in Figure 3A. This result shows that a p-type ZnO layer with high optical purity can be grown by RF sputtering deposition at high temperature. The p-type ZnO films that were reported in the previous studies did not show any near-bandedge emission at room temperature.$^{13}$ The p-type ZnO film shown in Figure 3A, however, also showed broad deep-level emissions at approximately 640 nm that can be attributed to oxygen-related defects.$^{14}$

Figure 3B shows an EL spectra of the homojunction ZnO LED, with a near-bandedge emission at 380 nm (3.26 eV) and broad deep-level emissions at approximately 640 nm. A comparison of this EL spectrum with the PL spectra of the p-type ZnO film suggests that the recombination of electrons and holes occurs mostly in p-type ZnO. The carrier diffusion lengths of the electrons in p-type ZnO and of the holes in n-type ZnO were estimated to be 290.2 and 97.8 nm, respectively. This again indicates that carrier recombination occurs mostly in the p-type ZnO region. Figure 3A and B shows that
the intensity ratio of near-bandedge emission to deep-level emission is smaller in the EL spectrum than in the PL spectrum. This can be attributed to the absorption of near-bandedge emission by the defect-related deep levels in the p-type ZnO film during the escape of UV light from the p–n junction. Figure 3B also shows that the deep-level emission is increased in intensity and blue-shifted with increasing injection current. The blue-shift of deep-level emission is believed to result from the saturation of the lowest energy levels.\[15\]

We also found that the intensity of the near-bandedge emission could be enhanced and the deep-level emission suppressed when (Mg,Zn)O films were inserted in the n-type ZnO layer as energy barrier layers to confine the carrier recombination process to the high-quality n-type ZnO layer. Because the incorporation of Mg into ZnO increases the bandgap and the conduction band offset, the (Mg,Zn)O film can act as a large energy barrier for electrons and a low energy barrier for holes, as shown in the band diagram of Figure 4A.\[16\] The composition of the alloy film was determined to be Mg\(_{0.1}\)Zn\(_{0.9}\)O from the bandgap energy of 3.51 eV, which was obtained by PL measurement at room temperature.\[17\] As shown in Figure 4B, a ZnO LED with two 40 nm thick Mg\(_{0.1}\)Zn\(_{0.9}\)O films as the carrier confinement layers and a 40 nm thick n-type ZnO layer as the active region was grown on c-Al\(_2\)O\(_3\). Figure 4C shows EL spectra of the ZnO LED with Mg\(_{0.1}\)Zn\(_{0.9}\)O layers operated at forward currents of 20 and 40 mA. With increasing injection current, a red-shift of the bandedge emission was observed because of bandgap narrowing caused by heat generation. Unlike the case of the homojunction ZnO LED, the deep-level emission was not blue-shifted. This result indicates that the deep-level emission is from the p-type ZnO excited by UV light emitted from the confined n-type ZnO layer that does not show any deep-level emission in the PL spectrum. Figure 4D compares EL spectra from the homojunction ZnO LED and the ZnO LED with Mg\(_{0.1}\)Zn\(_{0.9}\)O layers. Both spectra exhibit near-bandedge emission peaks at 380 nm. It is noted that the deep-level emission peak is greatly suppressed in the LED with Mg\(_{0.1}\)Zn\(_{0.9}\)O carrier confinement layers compared to the LED without barrier layers. If the carrier recombination occurs in the p-type ZnO at the p-ZnO/Mg\(_{0.1}\)Zn\(_{0.9}\)O heterojunction interface, as in the case of p-ZnO/n-GaN,\[18\] the bandgap energy may be changed but still show very strong defect-related emissions from the p-type ZnO. Therefore, the insertion of two Mg\(_{0.1}\)Zn\(_{0.9}\)O barrier layers enabled the confinement of the carrier recombination in the high-quality n-type ZnO between the two barrier layers, suppressing the defect-related peaks from the heterojunction ZnO LED, and increasing the EL intensity of bandedge emission by about 55 % compared to the homojunction ZnO LEDs. This result clearly shows that the insertion of two Mg\(_{0.1}\)Zn\(_{0.9}\)O barrier layers improves the near-bandedge EL emission by confining the carriers to the high-quality n-type ZnO well layer.

In summary, we demonstrated the operation of a UV-light-emitting ZnO homojunction LED by growing P-doped p-type ZnO on Ga-doped n-type ZnO. The ZnO LED emitted 380 nm UV light at room temperature and showed clear rectification with a threshold voltage of 3.2 V. The intensity of near-bandedge emission was further increased and the deep-level emission was greatly suppressed by using Mg\(_{0.1}\)Zn\(_{0.9}\)O layers as energy barrier layers to confine the carriers to the high-quality n-type ZnO.

**Experimental**

We used a balanced magnetic source with a grounded substrate because it can yield highly c-axis-oriented ZnO films.\[19\] We also used a high magnetic field to enhance the ionization, dissociation, and excitation of oxygen in the plasma and to decrease the oxygen vacancies in deposited ZnO films. A home-made heater with halogen bulbs was used for the high-temperature process and a water-cooled chamber wall was employed to minimize the outgassing. Epitaxial Ga-doped n-type ZnO layers of 1.5 nm thickness were grown on a c-Al\(_2\)O\(_3\) sub-
stratate by RF sputtering deposition at 900 °C, using a ZnO target mixed with 1 wt % Ga2O3. For the p-n homojunction ZnO LED, a layer of p-type ZnO with a thickness of 0.4 μm was grown in situ on the n-type ZnO layer at 900 °C using a ZnO target mixed with 1 wt % Ga2O3. For the p–n homojunction ZnO LED, two Mg0.1Zn0.9O epitaxial layers, each of 40 nm thickness, were deposited by co-sputtering MgO and ZnO targets on n-type ZnO. The RF power ratio for the MgO and ZnO targets was 1:4. The samples were subjected to a rapid thermal annealing (RTA) process for 5 min at 800 °C in a nitrogen atmosphere, in order to activate the p-type ZnO layers. A ZnO-based LED with a size of 300 μm × 300 μm was fabricated by etching the surface of the p-type ZnO layer with a 1 % aqueous HCl solution until the n-type ZnO layer was exposed for an n-type electrode pad to be formed. Ohmic contacts to the n-type and p-type ZnO layers were made from Ti/Au (30/80 nm) and NiO/Au (30/80 nm), respectively, by electron-beam evaporation.

Hall effect measurements were carried out in the van der Pauw configuration using a commercial system (BIO-RAD HIL5000PC). Photoluminescence (PL) spectra of n-type and p-type ZnO films, which were separately grown on c-Al2O3 substrates with 1 μm thick undoped ZnO buffer layers, were obtained at 300 K using a He–Cd laser (λ = 325 nm) as an excitation source. The I–V characteristics were measured at room temperature using a HP 4155 parameter analyzer and EL spectra were measured using a UV-vis spectrometer (USB2000-UV-VIS Fiber Optic Spectrometer, Ocean Optics Inc.).

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