Improved electroluminescence from n-ZnO/AlN/p-GaN heterojunction light-emitting diodes

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n-ZnO/p-GaN heterojunction light-emitting diodes with and without a sandwiched AlN layer were fabricated. The electroluminescence (EL) spectrum acquired from the n-ZnO/p-GaN displays broad emission at 650 nm originating from ZnO and weak emission at 440 nm from GaN, whereas the n-ZnO/AlN/p-GaN exhibits strong violet emission at 405 nm from ZnO without GaN emission. The EL intensity is greatly enhanced by inserting a thin AlN intermediate layer and it can be attributed to the suppressed formation of the GaO_x interfacial layer and confinement effect rendered by the AlN potential barrier layer. [doi:10.1063/1.3430039]

ZnO, with a large direct band gap of 3.37 eV and high exciton binding energy of 60 meV, is a promising material for ultraviolet (UV) light emitting diodes (LEDs) and laser devices.[1–3] Although ZnO-based p-n homojunction LEDs have been fabricated and weak electroluminescence (EL) was obtained,[4–6] ZnO still suffers from the lack of a reproducible, high-quality, p-type epitaxial growth technology, which seriously hampers the progress of ZnO homojunction LEDs. As an alternative approach, heterostructured LEDs have been demonstrated by growing n-type ZnO on top of a variety of p-type layers.[7–9] Most experiments on ZnO heterojunction LEDs have focused on p-GaN[10–14] or p-AlGaN substrates[15] because of their similar physical properties. Some researchers have fabricated n-ZnO nanowires (NWs)/p-GaN hybrid LEDs by various approaches such as hydrothermal approach[10] and chemical vapor deposition (CVD).[11,12] Such devices show obvious blue violet emission due to the confinement effect of NWs and low density of interface defects. However, the procedures to fabricate n-ZnO NWs/p-GaN hybrid LEDs are relatively complex and cannot be controlled easily. On the other hand, there have been attempts to fabricate n-ZnO film/p-GaN LEDs by other approaches such as radio frequency (rf) sputtering[13] and molecular beam epitaxy.[14] However, emission from the ZnO film/p-GaN LEDs is usually very weak due to the formation of nonradiative centers at the interface.[12–14] Recently, wide band gap MgO with high stability has been introduced into n-ZnO film/p-GaN LEDs to improve the device performance.[14] Alternatively, AlN, with the widest direct band gap (6.2 eV) among III-nitride semiconductors, has outstanding physical and chemical properties including high thermal conductivity, high stability, and good lattice match with ZnO and GaN. Therefore, it is possible to adopt AlN to improve the performance of n-ZnO film/p-GaN LEDs. In this study, significant improvement of EL is observed when a 20 nm AlN intermediate layer is inserted into n-ZnO film/p-GaN LEDs. It can be ascribed to the suppression of the formation of the GaO_x layer and confinement effect of the AlN potential barrier layer.

The Mg-doped p-GaN films were grown on c-plane sapphire by metal-organic CVD, and the hole concentration and mobility were 2.8×10^{17} cm^{-3} and 12 cm^2/V s, respectively. For the n-ZnO/AlN/p-GaN structures, a 20 nm thick AlN layer was first deposited by rf sputtering of an Al target in Ar and N_2 mixed ambient on a p-GaN layer at 750 °C, followed by deposition of a 450 nm ZnO film at the same temperature. For comparison, the n-ZnO/p-GaN LED without an AlN layer was also fabricated under the same conditions. The undoped ZnO films exhibited n-type conductivity, and the electron concentration and mobility were 1.5×10^{18} cm^{-3} and 20 cm^2/V s, respectively. I–V measurements were carried out on a Keithley 2400 source meter. Photoluminescence (PL) spectra were excited by a He–Cd laser (325 nm) at room temperature (RT), while RT EL measurements were performed by a Hitachi F4500 fluorescence spectrophotometer. The x-ray photoemission spectroscopy (XPS) measurements were carried out on a PHI 5802 instrument with Al K_α (1486.6 eV) as the x-ray radiation source, and the detailed procedures can be found in our previous report.[16] Scanning electron microscopy (SEM) was performed on a JEOL-7001F field emission microscope equipped with energy dispersive x-ray spectroscopy (EDX). X-ray diffraction (XRD) measurements were carried out on a Bruker D8 diffractometer with Cu K_α radiation.

Figure 1(a) shows the cross sectional SEM image of the n-ZnO/AlN/p-GaN film. A three-layer structure of n-ZnO/AlN/p-GaN can be clearly observed and the thicknesses of ZnO and AlN are estimated to be 450 nm and 20 nm, respectively. The EDX spectrum of the n-ZnO/AlN/p-GaN structure shown in Fig. 1(b) reveals the existence of the corresponding elements. To investigate the crystallinity in the AlN layer, the XRD pattern of a 200 nm thick AlN film on p-GaN/sapphire prepared under the same conditions is

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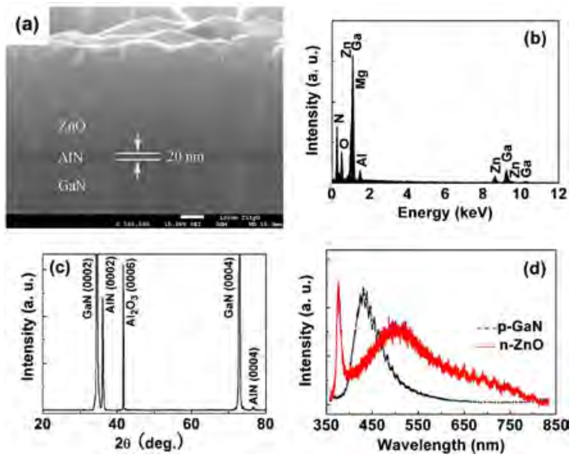

FIG. 1. (Color online) (a) Cross-sectional SEM image of n-ZnO/AlN/p-GaN, (b) EDX spectrum of n-ZnO/AlN/p-GaN, (c) XRD pattern of the AlN film on GaN/sapphire, and (d) PL spectra of p-GaN and n-ZnO.

shown in Fig. 1(c). It can be seen that the AlN thin film is grown along a c-axis orientation and has a AlN(0002)//GaN(0002) epitaxial relationship with GaN due to their similar lattice parameters.[17] The PL spectra obtained from both the ZnO and GaN layers are depicted in Fig. 1(d). The PL spectrum of the Mg-doped GaN film shows a blue emission band centered at 430 nm, which is generally attributed to the deep donor to acceptor transition of Mg-related complexes.[18] The PL spectrum of ZnO reveals a significant UV emission peak at 376 nm corresponding to the near band edge emission as well as a weak broad, defect-related emission from 400 to 700 nm with the peak centered at 505 nm (2.45 eV), which is due to the defect emission related with oxygen vacancies or zinc interstitials.[1–3]

Figure 2 shows the I–V characteristics of heterojunction devices with and without the AlN potential barrier layer. Both samples demonstrate a nonlinear rectifying behavior while an additional voltage drop across the AlN layer is observed from the n-ZnO/AlN/p-GaN device. The linear curves in the inset of Fig. 2 from both the Au/Ni on p-GaN and Au/Ti on n-ZnO reveal good Ohmic contacts at both electrodes, inferring that the rectifying behavior of the LEDs originates from the n-ZnO/p-GaN heterojunction.

The EL spectra of the n-ZnO/p-GaN and n-ZnO/AlN/p-GaN heterojunction diodes under various currents are shown in Figs. 3(a) and 3(b), respectively. As shown in Fig. 3(a), the EL spectrum of n-ZnO/p-GaN diode displays broad red emission at around 650 nm and weak blue emission at 440 nm. By comparing the PL spectra, it can be easily identified that the 440 nm emission originates from the deep level recombination in the p-GaN layer. The slight redshift can be ascribed to the heating effect in the device.[19] However, the emission at 650 nm is quite different from that in the PL spectra of the n-ZnO and p-GaN layers, and its origin will be discussed in details later. According to Fig. 3(b), the n-ZnO/AlN/p-GaN diode exhibits strong violet emission at 405 nm with absence of deep level emission. This peak has been observed frequently from the EL spectra of ZnO-based LEDs and can be attributed to the transmission from the shallow donors to the valence band or the donor-acceptor pair recombination in ZnO.[3,4,14] The most important feature presented in this figure is that emission from n-ZnO/AlN/p-GaN is much stronger than that from n-ZnO/p-GaN even if the injected current in the n-ZnO/AlN/p-GaN is lower. The photographs of light emission from the devices shown in the inset of Figs. 3(a) and 3(b) demonstrate clearly the above results. Furthermore, the p-GaN:Mg films grown by molecular beam epitaxy (SVTA, Minnesota, USA) were also adopted for fabricating heterostructure LEDs and similar results were obtained (results not shown here).

It has been reported that the performance of ZnO/GaN heterostructure LEDs is strongly related to the interfacial layer.[12–14] To identify the nature of the interfacial layer, XPS depth profiles of the heterojunction and XPS core-level spectra at the interface were acquired and the corresponding results are shown in Fig. 4. A relatively clear interface between the ZnO and GaN can be observed from the XPS depth profile of ZnO (50 nm)/GaN heterojunction, as shown in Fig. 4(a). However, N diffusion from the GaN into ZnO layer is obviously observed at the interface, and the N atomic percentage is as high as 20% in ZnO. It has been reported that N can form a deep acceptor level energy (1.3 eV) in ZnO,[20] and thus the transition from the conduction band to the N-related deep acceptor level is possible. This may be the origin of the broad red emission (650 nm) observed from n-ZnO/p-GaN LEDs. It can also be found that the O concentration is higher than that of Zn at the interface close to the GaN layer, and O

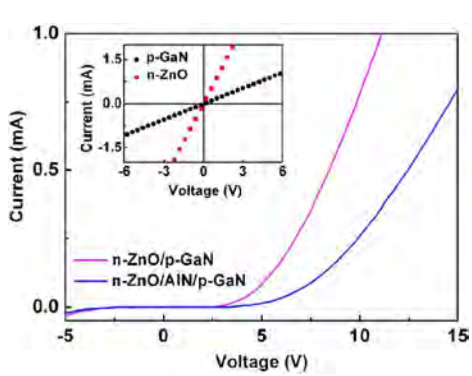

FIG. 2. (Color online) I-V characteristics of a n-ZnO/p-GaN LED and a n-ZnO/AlN/p-GaN LED. The inset shows the I–V characteristics of Au/Ni and Au/Ti metal contacts on p-GaN and n-ZnO films.

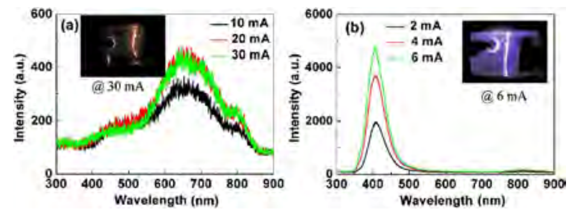

FIG. 3. (Color online) Room EL spectra of (a) a n-ZnO/p-GaN LED and (b) a n-ZnO/AlN/p-GaN LED under various currents and their EL images (inset).

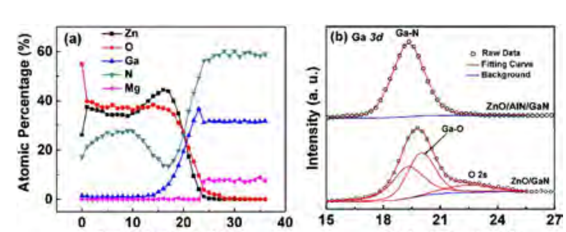

FIG. 4. (Color online) (a) XPS depth profile of a n-ZnO (50 nm)/p-GaN heterojunction, and (b) Ga 3*d* core-level XPS spectra at the interfaces of ZnO/GaN and AlN/GaN.

is found even when the Zn concentration is close to zero, implying that O atoms have diffused into the GaN layer. To identify the states of the Ga atoms in the GaN layer, the Ga 3*d* core-level spectrum was acquired from the ZnO/GaN interface. As shown in the lower curve in Fig. 4(b), in addition to the Ga–N bonding, Ga–O bonding exists indicating that the GaO_x interfacial layer forms at the interface of the ZnO/GaN. Actually, a GaO_x interfacial layer has also been identified by high resolution transmission electron microscopy.[13,21] For comparison, the Ga 3*d* core-level spectrum from the AlN/GaN interface of the ZnO/AlN/GaN structure is given in the upper curve in Fig. 4(b). Obviously, Ga atoms exhibit uniform Ga–N bonding states, indicating that the AlN intermediate layer is a good passivation layer. Therefore, the GaO_x interfacial layer may be responsible for the low intensity EL from the ZnO/GaN device by providing a high density of interface states acting as the nonradiative recombination centers.[13,22] After inserting a thin AlN layer, diffusion of O/N atoms is prevented by this intermediate layer and formation of the GO_x interfacial layer is suppressed. Therefore, the performance of the n-ZnO/AlN/p-GaN LEDs is improved significantly.

Besides the interfacial layer, band alignment has an important effect on the performance of the heterostructured LEDs since the carrier transport at the interface is determined by the band alignment.[16] Using the Anderson model, the conduction band offset (CBO) and valence band offset (VBO) of ZnO/GaN are determined to be 0.15 and 0.12 eV, respectively. The barrier heights for electrons and holes are almost the same. In this case, electrons drift from ZnO to GaN and equally, holes drift from GaN to ZnO under forward bias.[14] As a result, emissions from both the p-GaN and n-ZnO layers can be detected, but the emission intensity is considerably weak due to the high density of defects at the interface, which is consistent with our results. On the other hand, the CBO between ZnO and AlN is experimentally determined by XPS to be 3.29 eV while the VBO of 0.94 eV for AlN/GaN can be derived by the transitivity rule.[23] Thus, the energy barrier for electrons (3.29 eV) is much higher than that for holes (0.94 eV), indicating that the existence of AlN can effectively block electrons injection from ZnO to GaN in the n-ZnO/AlN/p-GaN LEDs with an AlN layer, whereas holes in the GaN layer can tunnel through the barrier and enter the ZnO layer due to the lower VBO and band bending under forward bias. Hence, recombination of carriers takes place in the ZnO layer and the emission intensity is remarkably enhanced due to the lower density of interface defects and accumulated electrons.

In summary, n-ZnO/p-GaN and n-ZnO/AlN/p-GaN heterojunction LEDs have been fabricated. The EL intensity is greatly enhanced after inserting a thin AlN intermediate layer into the device and it can be attributed to the suppression of the formation of the GaO_x interfacial layer and confinement effect rendered by the AlN potential barrier layer. The results will be helpful to the design of high efficiency n-ZnO/p-GaN heterojunction LEDs.

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