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The ultralow driven current ultraviolet-blue light-emitting diode based on *n*-ZnO nanowires/*i*-polymer/*p*-GaN heterojunction

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Under the ultralow driven current of 25 μA an ultraviolet (UV)-blue electroluminescence (EL) with a weak defect-related emission could be obtained for the n type (*n*-) ZnO nanowires (NWs)/ insulating (*i*-) polymer/p-type (*p*-) GaN light-emitting diode (LED). The *i*-MgO layer was also explored as a carrier blocking layer for the comparison. For the *i*-polymer inserted LED the EL emission peak was located at 400 nm, by analyzing the spectra it is believed that the emission includes several compound originations from both ZnO and GaN. The flexible carrier blocking layer, such as *i*-polymer, could effectively confine the radiative recombination zone. © *2010 American Institute of Physics*. [doi:10.1063/1.3505929]

Nowadays, many researchers have devoted to the ultraviolet (UV) optoelectronic devices. ZnO is a promising material for the short-wavelength photonic applications due to its direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV,[1] which make it a potentially useful photonic material for UV lasers, photodetectors,[2,3] and other optoelectronic devices.[4,5] Furthermore, ZnO has various one-dimensional (1D) nanostructures including nanowires (NWs), nanobelts, and nanorods. Because of the small size and high crystal quality, 1D ZnO nanostructures are used as building units to construct different nanodevices, such as nanolasers, nanodetectors, and nanosensors. Recently, many researchers have obtained ZnO NWs based light-emitting diodes (LEDs). Because of the difficulty of the *p*-type doping in ZnO and the small in-plane lattice mismatch between GaN and ZnO, *p*-GaN is usually used to fabricate the heterojunctional ZnO NWs/*p*-GaN LEDs. Although the device structures were similar, the electroluminescence (EL) bands for different methods grown ZnO nanostructures were quite different. For the ZnO NWs grown by the metal-organic chemical vapor deposition (CVD) method on *p*-GaN, Park *et al.*[6] observed two EL emission bands located at 450 and 560 nm, Jeong *et al.*[7] obtained an UV EL emission band located at 386 nm. And for the ZnO NWs grown by the CVD method, Fu *et al.*[8] obtained a blue EL emission band centered at 405 nm. Zhang *et al.*[9] observed a strong blue EL emission peak, in which the peak position shifted from 440 to 400 nm with increasing the forward bias. For the hydrothermal growth of ZnO NWs, Lai *et al.*[10] detected a blue EL emission band centered at 410 nm. For all the above experiments ZnO nanostructures were grown directly on the *p*-GaN wafer. And the driven currents of the different heterojunction diodes were always varied from several to tens even hundreds milliamperes. We think that the differences of the EL emissions are mainly due to the electrical properties of ZnO structures grown by different methods and the interface properties between ZnO and *p*-GaN. To distinguish the originations of the EL emissions in the *n*-ZnO/*p*-GaN heterojunction LED and improve the LED performance we introduced two kinds of *i*-layers between *n*-ZnO and *p*-GaN wafer. The ZnO NWs were grown on both *i*-layers inserted *p*-GaN wafer by the low temperature hydrothermal method. And the EL properties were further studied.

As shown in Fig. 1(a), when the MgO thin layer fabricated on the *p*-GaN wafer, the epitaxial ZnO NWs have aligned along the vertical direction assisted with ZnO thin film in a large scale. The average diameter of the hexagonal ZnO NWs is about 300 nm shown in the inset of Fig. 1(a). Meanwhile, as shown in Fig. 1(b), when the polymer was spin-coated on the *p*-GaN wafer, the obtained ZnO NWs have a random distribution with the average diameter of about 300 nm likewise. To explore the crystalline quality of the as-grown ZnO NWs, the room temperature (RT) PL spectra for ZnO NWs were performed (not shown here). For ZnO NWs grown on different substrates, the PL spectra are almost the same, which show a dominant sharp near band-edge emission at 388 nm with a full width at half maximum (FWHM) of 16 nm accompanied with a weak deep-level

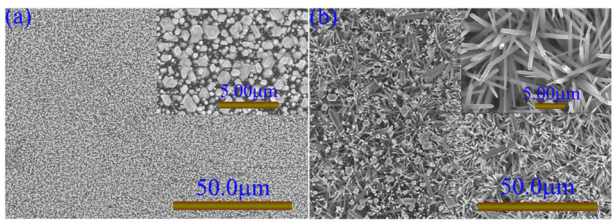

FIG. 1. (Color online) [(a) and (b)] SEM images of ZnO NWs fabricated on *p*-GaN wafer with *i*-MgO and *i*-polymer thin layers inserted, respectively, their magnified SEM images shown in the inset.

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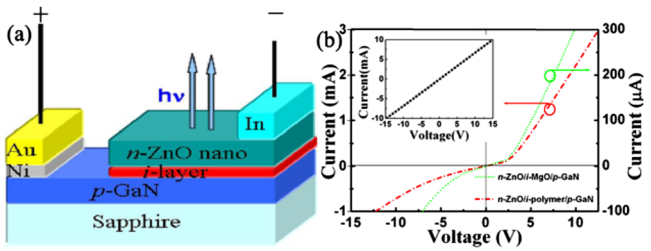

FIG. 2. (Color online) (a) Schematic diagram of *n*-ZnO nanostructures/*i*-layer/*p*-GaN heterojunction LED. (b) Current-voltage characteristics of *n*-ZnO/*i*-MgO/*p*-GaN and *n*-ZnO/*i*-polymer/*p*-GaN diodes, respectively. The inset shows current-voltage characteristic of Ni/Au Ohmic contact to the *p*-GaN.

emission at around 560 nm. The PL spectrum of *p*-GaN is dominated by a broad peak centered at about 420 nm, which is frequently observed in Mg-doped *p*-GaN corresponding to the transitions between conduction-band electrons or donors and Mg-related acceptors.[11]

The schematic diagram of the fabricated *n*-ZnO/*i*-layer/*p*-GaN heterojunction LED is shown in Fig. 2(a), the Ni/Au and In metals were used as electrodes for *p*-GaN wafer and *n*-ZnO nanostructures, respectively. Figure 2(b) shows the RT I-V characteristics of the *n*-ZnO NWs/*i*-MgO/*p*-GaN and *n*-ZnO NWs/*i*-polymer/*p*-GaN heterojunction LEDs. The *i*-MgO layer inserted LED demonstrates a nonlinear behavior with a similar forward turn-on voltage as that of the *i*-polymer inserted one. The I-V curve of the *n*-ZnO NWs/*i*-polymer/*p*-GaN heterojunction LED shows a typical back to back diode, the polymer layer acts as double Schottky diodes. Meanwhile, the injection current is much lower for the polymer inserted LED due to the polymer can be regarded as electron and hole blocking layer. The linear curve in the inset for Ni/Au on *p*-GaN reveals good Ohmic contacts have been formed in the electrodes, and In metal can form good Ohmic contact with *n*-ZnO reported everywhere. Therefore, the nonlinear behavior of the LEDs is considered originated from the *n*-ZnO NWs/*i*-layer/*p*-GaN. The EL spectra of the *n*-ZnO NWs/*i*-MgO/*p*-GaN and *n*-ZnO NWs/*i*-polymer/*p*-GaN heterojunction LEDs are shown in Fig. 3. The EL spectra of MgO inserted LED display a blue emission located at 420 nm and a broad orange-yellow defects related emission. By comparing the PL spectra, it can be easily identified that the 420 nm emission originates from the transition in *p*-GaN layer. And the broad emission band from 500 to 700 nm can be ascribed to the defects related emission in ZnO, which may be due to the interfacial defects formed among ZnO, MgO, and GaN. The emission originations will be further discussed in the following. The EL intensities for blue and defects related emissions are almost in

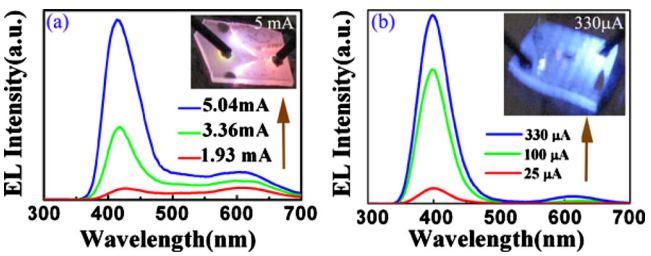

FIG. 3. (Color online) RT EL spectra of (a) *n*-ZnO/*i*-MgO/*p*-GaN and (b) *n*-ZnO/*i*-polymer/*p*-GaN LEDs under different forward injection current, the inserts show the corresponding EL images.

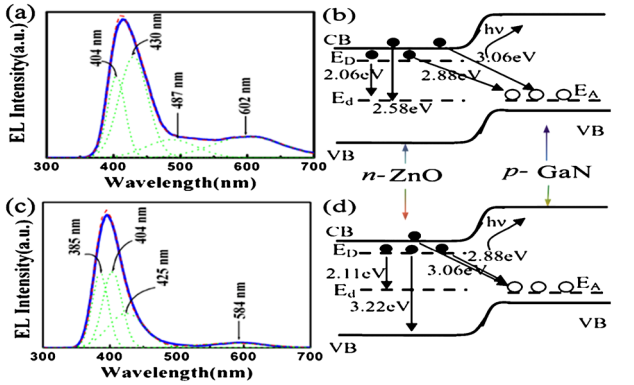

FIG. 4. (Color online) [(a) and (c)] The EL spectra and the Gauss analysis curves of *n*-ZnO/*i*-MgO/*p*-GaN LED and *n*-ZnO/*i*-polymer/*p*-GaN LED, respectively. [(b) and (d)] The corresponding energy band diagrams and transition processes responsible for the EL spectra.

the same order under a low forward injection current of 1.93 mA. With increasing the injection current to 3.36 mA, the blue EL emission dominates the spectrum accompanied with the relatively weak defects related emission. As shown in Fig. 3(b), the *n*-ZnO NWs/*i*-polymer/*p*-GaN LED exhibits the UV-blue emission located at 400 nm with weak defects related emission. The UV-blue emission peak which overlapped with the PL emission bands of ZnO and GaN can be considered as compound radiative transitions originated from ZnO, GaN, and the interface. The most obvious characteristic is that the UV-blue emission could be detected under an ultra low driven current of 25 μA, which is almost one order of magnitude lower than all the reported driven current data. With increasing the injection current to 330 μA, the EL emission peak position is unchanged and the corresponding intensity increases quickly. The photoimages of EL emission from the devices shown in the inset of Fig. 3 illustrate clearly the above results.

To further understand the originations of the EL emissions, the EL emission spectra are analyzed by Gauss fittings. And the corresponding transitions are illustrated by the energy band diagram for the better understanding. For each EL emission band the fitted four emission peaks could be obtained. As displayed in Fig. 4(a), the EL spectrum of the *n*-ZnO NWs/*i*-MgO/*p*-GaN LED under injection current of 5.04 mA can be divided into four individual peaks by the Gauss analysis. According to the reported results by other groups,[8,12] the fitted EL emission bands located at 404, 430, 487, and 602 nm could be attributed to the transitions from the conduction band edge of ZnO to the acceptor level of GaN, from the donor level E_D in ZnO to the acceptor level E_A in GaN, from the conduction band of ZnO to the defects level E_d in ZnO, from the donor level E_D to the defects level E_d in ZnO [as shown in Fig. 4(b)], respectively. For the *n*-ZnO NWs/*i*-polymer/*p*-GaN LED the main emission peak of the EL spectrum under injection current of 330 μA is comprised of a UV emission at 385 nm and a blue emission at 404 nm shown in Fig. 4(c). The EL emission located at 385 nm is ascribed to the near band gap excitonic emission in ZnO NWs as shown in Fig. 4(d). The weak EL emission at 584 nm could also be attributed to the transition from the donor level E_D to the defects level E_d in ZnO, due to the defects related emission is always a broad peak as reported everywhere. Another obvious characteristic is that the ratio of the UV emission intensity to that of the defects related

emission for the polymer inserted LED is always much larger than that of the MgO inserted one with increasing injection current. From this point of view, the interface defects for the polymer inserted LED are much less than that for the MgO inserted one.

The results of Chen *et al.*[13] showed that for the ZnO thin film/*i*-layer/*p*-GaN heterojunction the thickness of the *i*-layer determined the recombination zone in the LED. With the thicker *i* layer the recombination zone preferred at the ZnO side because of the efficient electron blocking property. In our experiment, the *i*-layers were quite thin, which was proposed to simulate the different interface properties between ZnO and GaN. By overall analysis of our experiment results and other reports for the ZnO/GaN heterojunction LED, the following conclusion could be drawn. (1) Because the electron mobility in ZnO is much higher than the hole mobility in GaN, the electrons have the high probability to transit from ZnO to GaN side through the interface or the thin *i* layer resulting the radiative recombination in GaN. (2) The EL emission of the heterojunction LED is the compound transitions composed with different originations from ZnO, GaN, and the interface. Due to the above two reasons, the EL spectra of ZnO/GaN heterostructure always show a broad emission band located in the UV-blue to visible regions and the dominated EL emission peaks are governed by the electronic properties of ZnO and GaN layers and the carrier blocking ability of the interfaces.

Our results also showed carrier blocking ability of the *i*-polymer is better than MgO, which induced the excitonic related EL emission of ZnO presented in the EL spectra. The other advantage of the polymer inserted LED is that the low driven current (microampere magnitude), compared with the tens or even several hundreds milliamperes threshold current for the ZnO/GaN LEDs reported by many papers.[6,7,12–16] The photoresist is usually used as an insulating layer in LEDs (such as the Refs. 17 and 18). And there are no reports about the luminescence from the photoresists. For the low-driven current property of the heterojunction LED, we believe the *i*-polymer plays an important role in the device. Referring to Refs. 16, 19, and 20, although the values of ΔEc are as high as 3.0 eV, the *i*-layers, such as SiO_2, AlN, and MgO, could not confine the electrons efficiently due to the mismatch, dislocation and stress could be easily formed. For the *i*-polymer inserted LED, ideal interfaces could be built for the well flexible properties. As a result, the dominant EL emission peaks are located at around 400 nm with a quite broad FWHM, which means the electrons could tunnel into the GaN layer and obtain radiative recombinations with holes. As a contrast, the *i*-polymer used in our experiment showed a better block for both of the carriers, which induced a quite low current under the same voltage compared with the MgO inserted device [Fig. 2(b)]. For the *n*-ZnO/*i*-polymer/*p*-GaN LED, the carriers could accumulate at the different interfaces by applying a forward voltage. When the electronic field applied on the devices is high enough, the carriers could tunnel through the thin polymer layer to generate luminescence with different emitting centers. Due to this reason the driven current is quite low for the *n*-ZnO/*i*-polymer/*p*-GaN LED. Considering the life time of the *n*-ZnO/*i*-polymer/*p*-GaN LED, The similar EL results were obtained through continuous EL measurements (1 h per time, two times per week) during two months.

In summary, using the polymer as the *i*-layer in *n*-ZnO NWs/*p*-GaN heterojunction LED the device showed a dominated UV-blue EL emission with very low driven current of microampere magnitude. By analyzing the EL spectra carefully, it is believed the originations of EL emission were the compound radiative transitions between ZnO and GaN layers. Ultralow driven current LED devices resulting in less thermal effects may have potential application prospect.

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