Ultraviolet electroluminescence from two-dimensional ZnO nanomesh/GaN heterojunction light emitting diodes

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The authors report the fabrication of heterojunction light emitting diodes (LEDs) based on two-dimensional (2D) hexagonal ordered *n*-type ZnO nanomesh and *p*-type GaN. The 2D ZnO nanomesh array was prepared by employing polystyrene spheres as a template. When a forward bias was applied to the LED, a strong ultraviolet (UV) electroluminescence peaked at 385 nm can be observed. The peak deconvolution revealed three emission peaks at 370, 388, and 420 nm. The origin of these emission peaks will be discussed. In addition, the LED was capable of exciting a red phosphor to convert UV light into red light. © *2011 American Institute of Physics*.
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Due to the direct wide band gap energy of 3.37 V and a large exciton binding energy of 60 meV, ZnO films have been considered as a potential material for ultraviolet (UV) light emitting diodes (LEDs),[1,2] laser sources,[3,4] and solar cells.[5] Among several materials, *p*-GaN is an ideal *p*-type substrate for ZnO-based LEDs because of the similar crystallographic between ZnO and GaN.[6,7] Nanostructured ZnO especially low-dimensional arrays, have attracted great interest and been widely investigated because of their special physical and chemical properties.[4] In the past years, many types of heterojunction LEDs based on one-dimensional ZnO nanowire/nanorod arrays and *p*-GaN substrate have been fabricated using various techniques such as hydrothermal approach[8] and chemical vapor deposition.[9,10] However, LEDs based on two-dimensional (2D) nanostructures are scarce. The 2D nanostructures is expected to improve the extraction efficiency of LEDs.[11] In this letter, we demonstrated a heterojunction LED based on large-area 2D hexagonal ordered *n*-type ZnO nanomesh and Mg-doped GaN as a *p*-type injector. The strong UV electroluminescence (EL) emission can be observed from the device. This approach provides an alternative route in fabricating nanoscale optoelectronic devices.

The Mg-doped *p*-GaN (0001) film grown on sapphire substrate was bought from Semiconductor Wafer Co. The schematic illustration of preparation process of 2D hexagonal ZnO nanomesh is shown in Fig. 1(a). First, the ordered monolayer of polystyrene (PS, size of 960 nm) spheres template was coated on *p*-GaN by self-assembly method.[12] Then *n*-type ZnO thin film was deposited on the template by filtered cathodic vacuum arc technique.[13] The arc was operated in dc mode with current of 50 A. The deposition temperature was 150 °C and the oxygen flow rate was 42 SCCM (SCCM denotes cubic centimeter per minute at STP). Finally, highly ordered 2D hexagonal ZnO nanomesh was obtained by dissolving PS in toluene. Scanning electron microscopy (SEM) was performed on a Philips XL 30 FEG SEM. Current-voltage (I-V) measurements were carried out on a Keithley 2400 SourceMeter and the EL spectra were measured by Ocean Optics USB4000 spectrometer. Low temperature photoluminescence (PL) measurements were performed using a He-Cd laser of 325 nm as the excitation source.

A low magnification SEM image of ZnO nanomesh is shown in Fig. 1(b), which indicates a large area (>1 cm^2) highly ordered hexagonal array of thin film. The upper inset is the high magnification image which shows that the pore size is about 700 nm and the neck width is around 95 nm. The lower inset is the cross-section view of the interface between ZnO nanomesh and GaN which indicates a sharp and smooth interface. The schematic diagram of the LED is shown in Fig. 1(c). The top of the ZnO nanomesh is

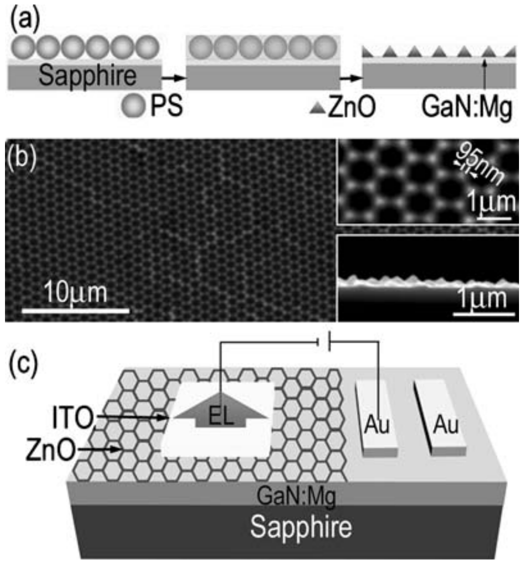

FIG. 1. (Color online) (a) Schematic illustration of the preparation of 2D hexagonal ordered ZnO nanomesh. (b) SEM image of the ZnO nanomesh. The upper inset is the high magnification SEM image of the sample. The lower inset is the cross-section view of the interface between ZnO nanomesh and GaN. (c) Schematic diagram of the LED device.

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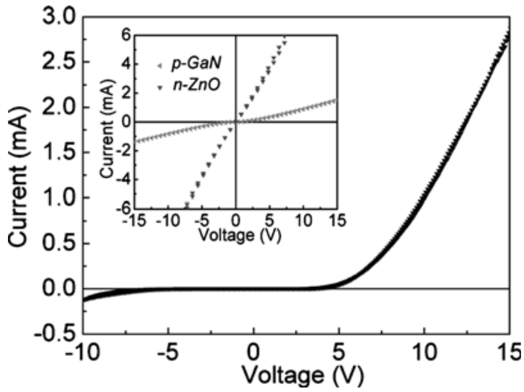

FIG. 2. (Color online) Room temperature I-V characteristics of the *n*-ZnO nanomesh/*p*-GaN heterojunction LED device. The inset shows the I-V characteristics of ITO on *n*-ZnO and Au on *p*-GaN.

contacted with an indium tin oxide (ITO) layer deposited on a transparent glass sheet which was used as an electrode. A gold electrode was deposited on the *p*-GaN to form Ohmic contact. The device area was about 15 mm × 8 mm.

Figure 2 shows the I-V characteristic of the 2D *n*-ZnO nanomesh array/*p*-GaN heterojunction LED device measured at room temperature, which demonstrates a good nonlinear rectification behavior. The linear curves in the inset of Fig. 2 are the current-voltage characteristics of ITO on *n*-ZnO as well as Au on *p*-GaN which revealed that Ohmic contacts have been formed in both electrodes. Thus, it can be deduced that the rectification behavior origins from the *n*-ZnO/*p*-GaN heterojunction. The turn-on voltage of the heterojunction is about 3.8 V, which is consistent with the ZnO band gap. Moreover, when the device is under reverse biased condition, there is low leakage current (∼0.5 μA) at voltage of − 5 V. The leakage current is smaller compared with the reported result,[14] indicating that the measured I-V characteristics of *n*-ZnO/*p*-GaN heterojunction showed diode characteristics.

Figure 3(a) shows the EL spectrum of the 2D *n*-ZnO nanomesh/*p*-GaN heterojunction LED device, which is measured under various forward bias voltages (10, 15, 20, 25, and 30 V) at room temperature. The EL spectrum showed a strong emission peak at 385 nm, and the full width at half-maximum intensity is 40 nm. The emission intensity is increased gradually as the forward bias voltage increase from 10 to 30 V. The profile of the EL spectrum does not change with the increase in the biased voltage. Moreover, no defect-related emissions can be observed in the spectrum which indicated the high-quality of the ZnO nanomesh. The inset of Fig. 3(a) displays a colored photo taken from the LED under forward bias voltage of 25 V, which was captured by a digital camera (Canon IXUS 9701S). The strong blue-light emission can be clearly seen by naked eyes even in normal lighting environment. More importantly, it is noted that only the region of *p*-GaN:Mg covered with the ZnO nanomesh exhibited the blue-light emission. The peak deconvolution of the spectrum with Gaussian functions is shown in Fig. 3(b), which indicates that the band consists of

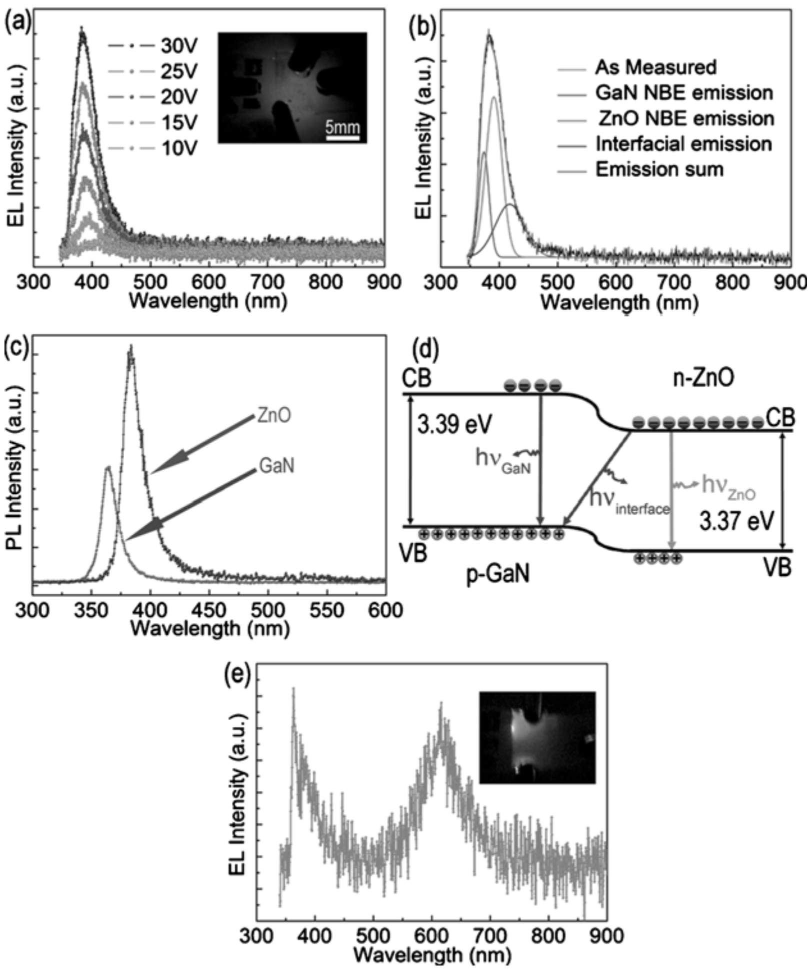

FIG. 3. (Color online) (a) The EL spectrum of the LED device under various forward bias voltages. The inset is a colored photo taken from the device under a forward bias voltage of 25 V. (b) Three distinct bands decomposed from broad UV emission by Gaussian deconvolution analysis. (c) PL spectra of *n*-ZnO nanomesh and *p*-GaN:Mg at room temperature. (d) Band diagram and transition process responsible for the EL in the *p*-*n* heterojunction diode. (e) The EL spectrum of the device coated by a red phosphor film. The inset is a colored photo taken from the phosphor coated LED.

three distinct peaks centered at around 370 nm, 388 nm, and 420 nm, respectively. The corresponding room temperature PL spectra of the *n*-ZnO nanomesh and *p*-GaN are shown in Fig. 3(c). The PL peaks for *n*-ZnO nanomesh and *p*-GaN are centered at 384 nm and 365 nm, respectively. Thus the emission peaks at 370 nm and 388 nm could be attributed to the near band edge emission from *p*-type GaN and *n*-ZnO nanomesh, respectively, which come from the recombination of free and bound excitons. In order to understand the origin of the EL emissions, the band structure diagram of the *n*-ZnO/*p*-GaN is shown in Fig. 3(d).[15,16] The electron affinities (χ) for ZnO and GaN are taken as 4.35 eV and 4.20 eV, respectively.[17] The band gap energies (E_g) of ZnO and GaN are presumed to be 3.37 eV and 3.39 eV at room temperature, respectively. The blue emission at around 420 nm could be attributed to the radiative interfacial recombination of electrons from the conduction band edge of *n*-ZnO and holes from the acceptor level of *p*-GaN.

It is known that UV light can be converted to visible light by exciting a phosphor. In order to show the strong EL emission from the LED, the device was coated by a layer of red phosphor film. The phosphors film was fabricated by mixing the red phosphor particles (TMR-500630 whose excitation wavelength is between 255 and 530 nm) with the epoxy. Figure 3(e) shows the EL spectrum from the red phosphor coated LED under a forward bias of 25 V. Besides the UV emission peak at 385 nm, a broad emission peak centered at 615 nm can also be observed. The strong red-light emission can be seen by naked eyes and the emission photo is shown in the inset of Fig. 3(e).

In summary, we demonstrated a heterojunction LED based on *n*-type ZnO nanomesh and *p*-type GaN. The heterojunction LED exhibited a strong EL emission peaked at 385 nm. The origin of the emission peak is attributed to the band edge emission from the ZnO nanomesh, GaN and interfacial recombination of electrons from the conduction band edge of *n*-ZnO and holes from the acceptor level of *p*-GaN. The heterojunction LED was capable of exciting a red phosphor and it can convert the UV emission into red emission.

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