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Near ultraviolet light emitting diode composed of *n*-GaN/ZnO coaxial nanorod heterostructures on a *p*-GaN layer

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The authors report on the fabrication and characteristics of near ultraviolet nanorod light emitting diodes (LEDs) composed of *n*-GaN/ZnO nanorod heterostructures on *p*-GaN substrates. The nanorod LEDs consist of the vertically aligned *n*-GaN/ZnO coaxial nanorod arrays grown on a *p*-GaN substrate. The LEDs demonstrated strong near ultraviolet emission at room temperature. The nanorod LEDs were turned on a forward-bias voltage of 5 V, and exhibited a large light emitting area. From electroluminescent spectra, dominant emission peaks were observed at 2.96 and 3.24 eV for an applied current of 2 mA. The origins of the strong and large area light emission are also discussed in terms of enhanced carrier injection from *n*-GaN nanostructures to *p*-GaN substrates.
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One-dimensional nanorod heterostructures which show compositional modulations along either the axial[1,2] or radial[3–5] direction offer the opportunity to design numerous novel structures for optoelectronic device applications. For example, embedding quantum structures in a single nanorod can confine both carriers and emitted photons efficiently in the nanorod as well as can tune the wavelength of emitted light.[6–9] Despite the successful fabrications of the nanorod heterostructures, nanodevice applications of the nanorod heterostructures have rarely been reported. Only a few studies have been reported about the use of the heterostructures as components of light emitting nanodevices and high electron mobility nanotransistors[7,10] and the practical use of the nanodevices has still remained out of reach. An individual manipulation of the nanostructures for nanodevice applications has been very difficult because of the necessary use of tedious and complicated *e*-beam lithography. In addition, only a limited number of nanorods have been utilized for most of nanorod device structures suggested to date, and the integration of nanorod devices is another huge obstacle.[11] Meanwhile, the individual manipulation and integration of nanostructures are not always necessary for many device applications. Even a bundle of nanorods can be more useful for practical device applications: a bundle of homogeneous ZnO nanorods yielded large-scale device applications including light emitting devices[12] (LEDs) and solar cells.[13] Nevertheless, the use of nanorod heterostructures for practical device applications has not been tried, presumably because it is very difficult to prepare vertically aligned nanorod heterostructures on many different substrates. Here, we report on the fabrication of vertically aligned GaN/ZnO nanorod heterostructures on *p*-GaN substrates and their ultraviolet (UV) LED applications.

Nanorod LEDs consist of the vertically aligned *n*-GaN/ZnO coaxial nanorod arrays grown on a 2-μm-thick *p*-GaN layer coated on *c*-Al_2O_3; the schematic is shown in Fig. 1(a). At the first stage, vertically aligned ZnO nanoneedles were prepared as a core nanomaterial by using diethylzinc and oxygen as the reactants.[14] After the preparation of ZnO nanoneedles, GaN layers were epitaxially grown on the ZnO nanoneedles by using metal organic vapor phase epitaxy in order to fabricate the coaxial nanorod heterostructures. For the heteroepitaxial growth of GaN on ZnO nanoneedles, trimethyl Ga (TMGa) and ammonia were employed as the reactant sources and hydrogen was the carrier gas.[15] Typical flow rates of TMGa and ammonia were 3.0 and 1000 SCCM (SCCM denotes standard cubic centimeter per minute of STP), respectively. The growth temperature was in the range of 500–650 °C.[15] Meanwhile, field-emission-gun scanning electron microscopy (FEG-SEM) clearly reveals the morphology of the nanoneedle arrays at each stage. As shown in Fig. 1(b), the ZnO nanoneedles exhibited uniform distributions in their diameters and lengths and the number density of nanoneedles was as high as 10^{10} cm^{-2}. Figure 1(c) exhibits the change in the morphology of nanorods after a GaN thin layer was coated on ZnO nanoneedles: the mean diameter of the nanorods increased from 40 to 52 nm due to the deposition of a GaN layer for 3 min. Moreover GaN/ZnO nanorod heterostructures in this study exhibited a very good vertical alignment in contrast to our previous report,[15] facilitating nanorod LED fabrications. Nanorod

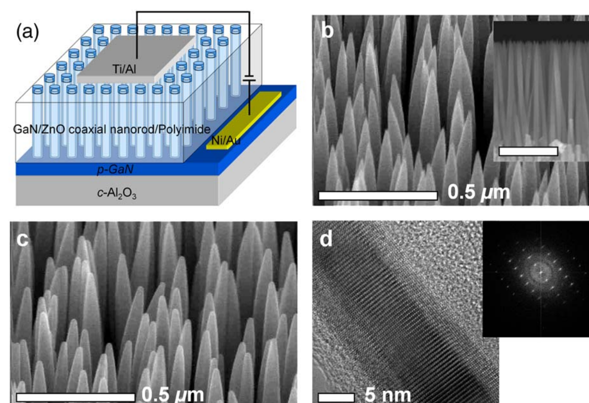

FIG. 1. (Color online) (a) Schematic illustration of a GaN/ZnO coaxial nanorod heterostructure on *p*-GaN. (b) FEG-SEM image of ZnO nanoneedle arrays grown on *p*-GaN. ZnO nanoneedles are well aligned perpendicular to the *p*-GaN surface. (c) SEM image of GaN/ZnO coaxial nanorod heterostructure. (d) HR-TEM image of GaN/ZnO coaxial nanorod heterostructures.

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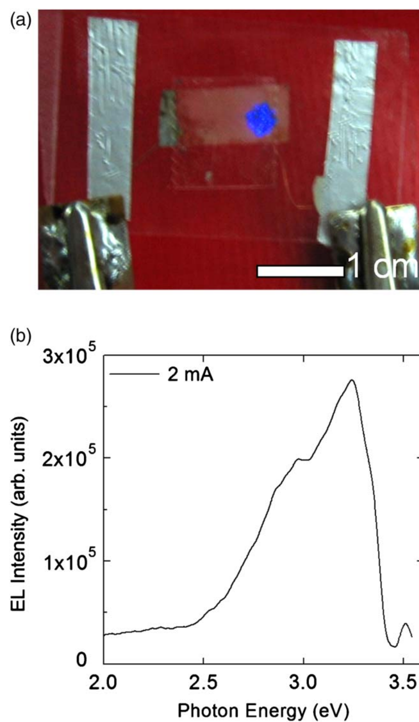

FIG. 2. (Color online) (a) Photograph of light emission from the EL device at a bias voltage of 2 mA. The electroluminescence was strong enough to be clearly observed with naked eyes. (b) Room temperature EL spectra of the nanorod LED based on *n*-GaN/ZnO coaxial nanorods grown on *p*-GaN.

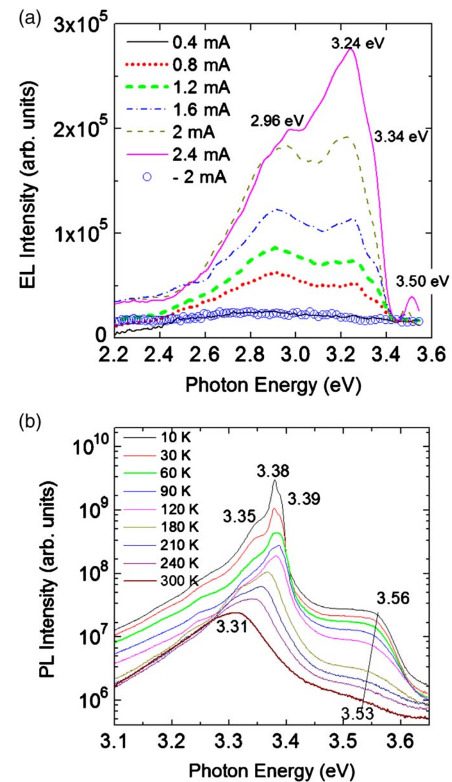

FIG. 3. (Color online) (a) Room temperature EL spectra of a *n*-GaN/ZnO coaxial nanorod array on *p*-GaN heterojunction device at various applied current levels. (b) Temperature-dependent PL spectra of GaN/ZnO coaxial nanorods.

LEDs were fabricated by metallization on *n*-GaN/ZnO coaxial nanorod heterostructures and *p*-GaN. The Ohmic contact on *p*-GaN was fabricated by evaporating Ni and Au bilayers.[12] The typical Ni and Au thicknesses were 100 and 500 Å, respectively. After the metallization of *p*-GaN, the empty gaps between the individual GaN/ZnO nanorods were filled with a solution of polyimide and nanorod tips were exposed by a simple plasma treatment.[12] For the metallization of *n*-GaN/ZnO nanorods, Ti(100 Å)/Al(500 Å) bilayers were deposited on the nanorod tips through a shadow mask by electron-beam evaporation, resulting in a continuous contact layer on GaN/ZnO nanorods as shown in Fig. 1(d). Good Ohmic contacts on both GaN/ZnO and *p*-GaN were made by rapid thermal annealing at 500 °C for 1 min in N_2 and O_2, respectively.

Uniform coating and heteroepitaxial growth of a thin GaN layer on ZnO nanoneedles were confirmed by high resolution transmission electron microscopy (HR-TEM). As shown in Fig. 1(d), a thin GaN layer with a 7 nm thickness was uniformly coated on the entire surface of ZnO nanorods, and the interface between ZnO and GaN was abrupt and semicoherent. Meanwhile, the inset of Fig. 1(d) shows the electron diffraction pattern of a GaN/ZnO coaxial nanorod heterostructure obtained by fast Fourier transform. The diffraction pattern is indexed as a [100] zone axis of hexagonal wurtzite GaN and ZnO, the evidence of the heteroepitaxial growth of GaN on ZnO nanoneedles. Indeed these results indicate that a thin GaN layer was heteroepitaxially and uniformly grown on the sidewalls of the vertically aligned ZnO nanorods, similar to the previous report on the GaN/ZnO nanorod heterostructures grown with random directions from the substrate.[15] Since the nanorod heterostructures were grown heteroepitaxially as well as vertically from the *p*-GaN substrate, these heterostructures offer an easy way to make good Ohmic contact on the *n*-type nanorod heterostructures.

Nanorod LEDs utilizing the nanorod heterostructures clearly demonstrated strong light emission when a current of 2 mA was applied to the LED. As shown in Fig. 2(a), the color of the electroluminescence was blue and violet, and the light emission was so strong that it was observed clearly with naked eyes even under normal room illumination condition. Compared with the previous report on EL emission from LEDs based on *n*-ZnO nanorods on *p*-GaN,[12] the light emission intensity was much stronger and the peak position was blueshifted. In addition, the emission intensity steadily increased with the current level up to 5 mA, and neither degradation nor significant variation in the current and emission intensity was observed during the continuous operation for several days.

The color of light emission was further investigated by measuring the electroluminescent (EL) spectrum of the nanorod LED as shown in Fig. 2(b). For the applied voltage of 6 V, the dominant EL emission was observed at 2.9 eV (430 nm) and 3.24 eV (382 nm) with a weak emission peak at 3.48 eV, different from those at 2.2, 2.8, and 3.35 eV from the *n*-ZnO/*p*-GaN LED.[12] The suppression of the EL emission at 2.2 eV and enhancement of the blue emission by GaN coating on ZnO nanorods imply that the carrier injection may occur between *p*-type Mg-doped GaN films and *n*-type GaN nanotubes rather than ZnO nanorods in the nanorod heterostructures.

For the further investigation of the EL emission peaks, EL spectra from the nanorod LED were measured at various applied current levels from −2 to 2.4 mA. As shown in Fig. 3(a), a very weak luminescence centered at 2.9 eV was observed for a small forward current of 0.4 mA and a reverse

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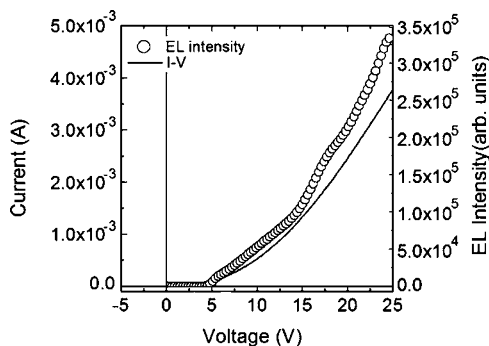

FIG. 4. Integrated emission intensity of the EL spectrum and current as a function of the applied bias voltage.

current of −2 mA. However, two additional EL peaks appeared at 3.24 eV (382 nm) and 3.50 eV (353 nm) as the driving current increased to 0.8 mA. For higher current levels up to 2.4 mA, all three EL peaks were commonly observed with changed EL peak intensities: the EL peaks at 2.9 and 3.24 eV were dominant for current levels below and above 1.6 mA, respectively.

As for the origins of the EL peaks, the EL emission at 2.9 eV is tentatively attributed to the transition between residual donors and Mg-associated deep acceptors in the *p*-GaN film because a similar photoluminescence (PL) peak was observed from room temperature PL spectra of *p*-GaN.[16] The UV emission peak around 380 nm is associated with shallow donors in the *n*-type GaN/ZnO nanostructures because the energy of 3.24 eV is smaller than the band-to-band transition of either GaN or ZnO. The shallow level defects may be formed unintentionally during the growth of GaN on ZnO nanorods.

Carrier confinement in semiconductor heterostructures is very useful for the fabrication of high efficiency LEDs.[17] Since the thickness of GaN layers was as small as 7 nm, carriers and excitons can be confined in the thin GaN layer. Figure 3(b) shows PL spectra of GaN/ZnO nanorod heterostructures measured at various temperatures from 10 to 300 K. The PL spectra of GaN/ZnO coaxial nanorod heterostructures show a dominant PL peak at 3.38 eV (367 nm) with a shoulder at 3.56 eV (348 nm), corresponding to the band-to-band transition of ZnO and GaN, respectively.[18] However, the PL peak from GaN was slightly blueshifted by 80 meV and strongly agrees well with a simple theoretical calculation based on a simple square well potential.[19] This result strongly supports that the blue-shift of the PL peak by 80 meV is caused from the quantum confinement effect in a thin GaN layer with a thickness of 7 nm.

Electrical characteristics of the nanorod LEDs were also investigated by measuring current-voltage (*I-V*) characteristic curves on the LEDs. The *I-V* curves clearly exhibited nonlinear and rectifying behavior with a turn-on voltage of ~5 V and a leakage current of $\sim 1\times 10^{-5}$ A at −5 V. For the forward-bias voltage at 5 V, both current and light emission intensity began to increase rapidly with the bias voltage, resulting from electron transport involving tunneling through the heterojunction (see Fig. 4). The turn-on voltage in the *I-V* characteristic curves is almost the same as that in the EL characteristic, clearly indicating that EL emission process involves the carrier transport through this *p*-*n* heterojunction of GaN. Furthermore, the light emitting efficiency can be enhanced because of the increased carrier injection rate through nanosized contacts at the junction interface between *n*-GaN/ZnO nanostructures and a *p*-GaN film, similar to the previous reports.[20] Especially carriers confined in the thin GaN layer may also contribute to enhancement of the carrier injection from the *n*-GaN nanostructures to *p*-GaN thin films.

In conclusion, LEDs based on GaN/ZnO coaxial nanorod heterostructures demonstrated a strong emission at near UV range. The nanorod LEDs were turned on a forward-bias voltage of 5 V, and exhibited strong emission from a large light emitting area. From EL spectra, dominant emission peaks were observed at 2.96 and 3.24 eV for an applied current of 2 mA. The strong and large area light emission at near UV may be caused by the enhanced carrier injection from *n*-GaN nanostructures to *p*-GaN substrates due to quantum confinement effect in the *n*-GaN nanostructures. The fabrication method of the high efficiency nanorod LEDs using nanorod heterostructures can simplify the LED fabrication process, which can reduce the cost for device fabrications with a high yield of device production. More generally, coaxial nanorod heterostructures can be employed for fabrications of many other optoelectronic devices including solar cells.

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