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Flexible Inorganic Nanostructure Light-Emitting Diodes Fabricated on Graphene Films

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Organic materials^[1,2] and amorphous films^[3] have long been studied for foldable and wearable mobile devices since the devices must be fabricated on a flexible plastic film. However, higher device performance is expected using a singlecrystalline inorganic compound semiconductor, such as gallium nitride (GaN), because of its high radiative recombination rate and mobility, as well as its excellent thermal and mechanical characteristics.^[4] Nevertheless, the high growth temperatures of single-crystalline inorganic semiconductors make it difficult to use a conventional plastic substrate with a low melting temperature. In addition, a continuous, rigid inorganic film has little tolerance for mechanical deformation. Although such problems can be circumvented by using assembly methods of micrometre-scale inorganic devices,^[5-7] complicated processes including many lithography and etching steps are required for fabricating and assembling the devices. These obstacles can be overcome basically using inorganic nanostructures grown on graphene films, which exhibit high temperature compatibility and good mechanical flexibility. Here, we report on the fabrication of flexible inorganic light-emitting diodes (LEDs) using GaN/ZnO coaxial nanorod heterostructures grown directly on graphene films and their reliable operation.

The basic strategy for the heteroepitaxial growth of GaN/ ZnO coaxial nanorod heterostructures on graphene films and

DOI: 10.1002/adma.201102407

the fabrication of flexible LEDs is illustrated schematically in Figure 1. First, large graphene films were synthesized on metal foils using chemical vapor deposition (CVD) and transferred onto arbitrary substrates; we used a silicon (Si) substrate with a thin silicon oxide (SiO_2) layer in this experiment. Because the morphology and density of ZnO nanostructures are strongly influenced by the crystal quality and grain size of the graphene films we used graphene films synthesized on cupper (Cu) foil using CVD, which typically have a high crystal quality and large grain size^[8] (see Supporting Information, Figure S1). Although there were some variations in nanorod length and vertical alignment (Supporting Information, Figure S1a), ZnO nanorods were grown directly on graphene films with no additional seed layer, at a density of 10^8 – 10^9 cm⁻² and interdistance of $\approx 1 \mu m$, appropriate for fabricating isolated coaxial nanorod heterostructures. In contrast, when graphene films synthesized on a nickel (Ni) film were used as the growth substrate, the density of ZnO nanorods was too high to deposit both GaN and In_xGa_{1-x}N/GaN multiple-quantum-well (MQW) layers uniformly on the nanorods in the radial direction. Meanwhile, small-size graphene flakes prepared by mechanical exfoliation yielded too low a density of ZnO nanorods, which made it difficult to fabricate metal electrodes on the nanorod tips for nanostructure LED fabrication and reduced the electroluminescence (EL) intensity per area.

To fabricate coaxial nanostructure LEDs, n-GaN, $In_xGa_{1-x}N/GaN$ MQWs, and p-GaN layers were coated heteroepitaxially over the entire surfaces of the ZnO nanorods. **Figure 2**a shows a scanning electron microscopy (SEM) image of GaN-based coaxial LED nanostructures fabricated on graphene films. The hexagonal morphology of the wurtzite crystal structure is clearly seen, indicating that the individual nanostructures are single-crystalline. The diameter of the hexagonal nanostructures was typically in the range 300–800 nm, and the average length was $\approx 3 \mu m$.

The uniform formation of single-crystalline GaN and MQW layers along the radial direction of the nanorods was confirmed using transmission electron microscopy (TEM) analysis. The cross-sectional schematic illustration and scanning TEM (STEM) image shown in Figure 2b,c demonstrate that GaN p–n homojunction with three-period MQWs were formed coaxially on the sidewalls of the hexagonal GaN nanostructures, where the three bright lines with a fairly uniform thickness of 3.8 ± 0.2 nm correspond to $In_xGa_{1-x}N$ quantum well layers. In particular, as shown in the high-resolution TEM image (Figure 2d), the abrupt, clean interfaces between the GaN quantum barrier and $In_xGa_{1-x}N$ quantum well layers were obtained with no structural defects, such as dislocations or stacking faults. The

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Figure 1. Schematic illustration of the process used to fabricate flexible LEDs using GaN/ZnO coaxial nanorod heterostructures grown on graphene films. a) Schematic illustration of the heteroepitaxial growth of GaN/ZnO coaxial nanorod heterostructures on large-area graphene films. b) Schematic of the fabrication of the LED device and its transfer onto a flexible plastic substrate. The photograph shows the LED arrays on graphene films, floating in deionized water after the etching and lift-off processes.

corresponding diffraction pattern in the inset of Figure 2d, obtained through fast Fourier transform, showed distinct diffraction spots with sixfold rotational symmetry, corresponding to the {100} planes of a wurtzite crystal structure. Additionally, the high-resolution TEM image and corresponding diffraction pattern in Figure 2e obtained from cross-sectional TEM analyses along the longitudinal direction, showed the formation of single-crystalline three-period MQW layers on the {100} side-wall of the *c*-axis-grown GaN nanostructure, and the thicknesses of the In_xGa_{1-x}N quantum well and GaN quantum barrier were also estimated to be 4.0 ± 0.4 and 30 ± 3 nm, respectively. These TEM results provide strong evidence for the single crystallinity of the coaxial nanorod heterostructures fabricated on polycrystalline graphene films prepared by CVD methods.

Ni/Au-coated nanostructures

The homogeneous growth of single-crystalline coaxial nanorod heterostructures, composed of GaN p–n homojunction with $In_xGa_{1-x}N/GaN$ MQWs, on large graphene films enabled the fabrication of flexible LEDs. The basic approach for fabricating flexible LEDs is shown in Figure 1b. After growing coaxial nanorod heterostructures on graphene films, thin Ni/ Au layers were deposited on the p-GaN surfaces of the nanostructures using electron beam evaporation and sequent rapid thermal annealing, resulting in the formation of isolated ohmic contacts to individual nanostructures. Then, the gaps among the nanostructures were filled with an insulating, flexible polymer, and additional Ni/Au metal layers were deposited on top of the nanostructure-embedded layer to enable current spreading. As an essential step for creating a flexible device, the LED devices

fabricated on graphene films were transferred onto Cu-coated polyethylene terephthalate (PET) substrate by wet etching the sacrificial SiO₂ layer underneath graphene films and using lift-off (photograph in Figure 1b). Then, the LEDs were adhered to the Cu-coated PET substrate to make an electrical connection between the graphene film of the device and an insulating plastic substrate.

Cu-coated PET

The nanostructure LEDs transferred onto the plastic substrates exhibited good electroluminescent characteristics. As shown in the photograph of the 10-mA-driven LED (Figure 3a), the blue light emission was strong enough to be observed readily with the unaided eve under normal indoor illumination. The light was emitted only from the circular contact area with a diameter of 600 µm and became brighter on increasing the applied current. Furthermore, distinct light emission spots were observed in magnified optical microscopy images. Nonuniform emission was also observed by failure of electrical contacts to some of nanostructure LEDs. The emission intensities of the individual light spots increased gradually, while maintaining the number of light spots as the applied current increased. These light-emitting features strongly indicate that the nanostructure LEDs work individually as sub-micrometerscale light emitters.

Quantitative LED characteristics were investigated further by measuring power-dependent EL spectra and current–voltage (I-V) characteristic curves. Figure 3b shows the EL spectra at various applied currents from 1 to 10 mA. The dominant EL peak was observed at 490–493 nm, presumably from $In_xGa_{1-x}N/GaN$

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Figure 2. GaN-based coaxial LED nanostructures grown directly on graphene films. a) SEM images of GaN-based coaxial LED nanostructures grown on graphene films. Both high- and low-magnification SEM images were obtained at a tilting angle of 30°. b,c) Cross-sectional schematic views and STEM image of the coaxially formed GaN-based LED structures. d,e) High-resolution TEM images of the In_xGa_{1-x}N/GaN MQW layers and corresponding diffraction patterns obtained via fast Fourier transform.

MQWs. In addition to the dominant peak, a broad shoulder also appeared around ≈465 nm at currents above 2 mA, presumably resulting from non-uniform thicknesses and compositions of In_xGa_{1-x}N quantum well layers formed on the multifacetted nanorod surfaces.^[9,10] The nanostructure LEDs exhibited the typical rectifying behavior in the I-V characteristic curves (Figure 3c), with a turn-on voltage of ≈ 5 V and a leakage current of 5×10^{-4} A at -5 V (blue solid line). The turn-on voltage and leakage current of a nanostructure LED were slightly larger than those of a typical thin-film LED, presumably due to parasitic resistances existed in nanostructure LEDs, including the contact, junction, and shunt resistances. Nevertheless, above the turn-on threshold, both the current and integrated emission intensity (red open circles) increased simultaneously on increasing the applied bias voltage. These results indicate that the EL emission originates from the carrier injection and

radiative recombination in the p–n junctions with MQW layers of the nanostructure LEDs.

It should be noted that the internal quantum efficiency (IQE) of coaxial nanorod heterostructures grown on graphene films was estimated to be \approx 13% by measuring temperature-dependent photoluminescence spectra. This IQE value is comparable to the previously reported values of 6–14% for InGaN/GaN quantum well nanowires^[11] and much higher than \approx 0.1–5% for GaAs/InGaP nanowire heterostructures.^[12] In addition, we believe that the device performances, including emission efficiency and uniformity, can be further improved by optimizing the nanostructure growth and device fabrication processes.

To use the nanostructure LEDs in a flexible form, the device characteristics of the LEDs transferred onto Cu/PET substrates were evaluated under substrate bending. Figure 4 shows the light emission photographs, EL, and electrical characteristics at bending radii of ∞ , 5.5, and 3.9 mm. As shown in the photographs (Figure 4a), when the 13-mm-wide substrate was bent to widths as small as 10 and 7 mm, corresponding to bending radii of 5.5 and 3.9 mm, respectively, the LEDs at a fixed current of 10 mA reliably produced blue light emission, even when bent, without observable degradation. The EL spectra obtained at different bending radii (Figure 4b) showed no significant changes in the EL peak position and intensity, confirming that the flexible nanostructure LEDs maintained their optical characteristics on bending to radii of curvature of 3.9 mm. In particular, the absence of a shift in the EL peak on bending indicated that the strain applied to the active region in individual nanostructures is negligibly small because strain generally induces the changes in the luminescent spectra.^[13,14] As shown in Figure 4c, in addition, the I-V curves at different bending radii exhibited very similar rectifying behavior, without appreciable differences in the device parameters, such as the turn-on voltage or leakage current. This suggests that no serious mechanical damage or fracture occurred at the top electrode or the junctions between the nanostructures and graphene during the bending test.

In addition to flexibility, the reliability of the flexible LEDs was investigated by measuring EL and electrical characteristics on repeating up to 100 bending cycles. First, as shown in Figure 4d, the nanostructure LEDs exhibited almost identical EL spectra at a fixed current of 10 mA with repetitive bending, and the integrated emission intensities remained nearly constant over up to 100 bending cycles. In addition to the luminescent characteristics, the electrical characteristics were preserved with repetitive bending, exhibiting very similar rectifying I-V curves shown in the inset of Figure 4e. The key electrical device parameters plotted in Figure 4e, including the forward-bias voltage ($V_{\rm f}$) at 10 mA and the reverse current ($I_{\rm r}$) at -5 V, were not significantly degraded; V_f only increased slightly within a range of \approx 2% and I_r remained nearly constant value of \approx 5 × 10⁻⁴ A. All these characteristics of the nanostructure LEDs fabricated on graphene films demonstrate reliable operation in a flexible form.

The hybrid heterostructure, composed of 1D inorganic semiconductor heterostructures grown directly on graphene films, constitutes a new class of material system for developing unconventional inorganic optoelectronic devices in transferable, flexible, or stretchable forms,^[15] taking full advantage of both inorganic semiconductor nanostructures and graphene.



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Figure 3. Visible nanostructure LEDs on graphene films. a) Photograph and optical microscopy images of the light emission from the LED at different applied currents. b) Power-dependent EL spectra at applied currents of 1–10 mA. c) *I–V* characteristic curve of the LED (black solid line) and a plot of the integrated EL intensity (red open circles) as a function of the applied bias voltage. a.u., arbitrary units.



Figure 4. Flexible inorganic nanostructure LEDs. a) Light emission photographs at bending radii of ∞ , 5.5, and 3.9 mm. b) EL spectra and c) *I–V* characteristic curves as a function of the bending radius. d) Plot of the integrated emission intensities as a function of bending cycle. The inset shows the corresponding EL spectra. e) Plots of the forward-bias voltages (V_f) at 10 mA and the reverse currents (I_r) at 5 V as a function of bending cycle. The inset shows the corresponding *I–V* characteristic curves. All photographs and EL spectra are obtained at a fixed current of 10 mA. a.u., arbitrary units.

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www.advmat.de In addition to the excellent electrical and optical characteristics of the inorganic semiconductors, coaxial heterostructures enable further gains in device performance by enlarging the active volume and improving the light extraction or absorption in optoelectronic devices.^[9,12,16] In particular for nitride LEDs, the luminescence efficiency can be improved by reducing the quantum confined Stark effect on the non-polar *m*-plane sidewalls of the GaN nanostructure.^[17] Graphene films that have recently become available on a large scale have good optical transparency, electrical and thermal conductivities, and high temperature stability and mechanical flexibility.^[8,18,19] In particular, a hybrid structure with nanorods that have a very small contact area with the graphene exhibited remarkable endurance under flexural deformation.^[20] All of these features of coaxial nanorod heterostructures on graphene films provide significant opportunities for fabricating various optoelectronic devices, especially for flexible LEDs and solar cells.

In summary, flexible inorganic nanostructure LEDs were fabricated using high-quality GaN/ZnO coaxial nanorod heterostructures grown directly on graphene films. The nanostructure LEDs exhibited strong blue emission, even under room illumination. Furthermore, the LEDs fabricated on graphene films were readily transferred onto flexible plastic substrates, which operated reliably in a flexible form without significant degradation of the LED performance. More generally, we believe that the approach provides a general and rational route for developing many different inorganic optoelectronics in flexible or stretchable forms, with potential advantages in device performance and processing.

Experimental Section

CVD Growth of Graphene Films: Large-area, high-quality graphene films were synthesized on Cu foil using the CVD method.^[19] First, the Cu foil was inserted in a tubular quartz tube and heated to 1000 °C with an H₂ flow at 8 standard cubic centimeters per minute (sccm) at 90 mTorr. After reaching 1000 °C, while maintaining the flow rate and reactor pressure, the Cu foil was annealed for 30 min to increase the grain size from a few micrometers to ~100 µm. Then, high-quality graphene films were grown on the Cu foil for 30 min under a mixture of CH₄ and H₂ at flow rates of 24 and 8 sccm, respectively. During growth, the reactor pressure was maintained at 460 mTorr. Finally, the sample was cooled rapidly to room temperature (~10 °C s⁻¹) under flowing H₂ at a pressure of 90 mTorr.

MOVPE Growth of ZnO Nanorods and GaN-Based LED Structures: ZnO nanorods were grown directly on CVD-grown graphene films using catalyst-free metal-organic chemical vapor deposition (MOCVD). Before growing the ZnO nanorods, the graphene films were first prepared on 300-nm-thick SiO₂/Si substrates using standard metal etching and transferring methods.^[19] The supporting substrate underneath the graphene was not restricted to a specific material for growth; here, a Si substrate coated with a sacrificial SiO₂ layer was used to enable the subsequent transfer process. For ZnO growth, high-purity diethylzinc (DEZn) and oxygen were used as the reactants for Zn and O, respectively, and high-purity argon was used as the carrier gas. The flow rates of DEZn and oxygen were 20 and 40 sccm, respectively. The reactor pressure and temperature during the growth were maintained at 3 Torr and 650 °C, respectively. After growing the ZnO nanorods, GaN-based p-n homojunction LED structures with In_xGa_{1-x}N/GaN MQWs were grown heteroepitaxially on the surfaces of the ZnO nanorods. First, an n-GaN layer was deposited around the circumferences of the ZnO nanorods using a two-step growth method.^[21] After initially coating the surfaces



of the nanorods with GaN at a low temperature of 600 °C, an additional n-GaN layer was deposited immediately at a high temperature of 950 °C using silane as the doping source. Then, three-period $In_xGa_{1-x}N/GaN$ MQWs were grown at 760 and 850 °C, respectively. Finally, an Mg-doped p-GaN layer was deposited on the top of the GaN quantum barrier layer at 1000 °C, using biscyclopentadienyl magnesium as the doping source. For the overall GaN growth, high-purity trimethylgallium, trimethylindium, and ammonia were used as precursors, and high-purity hydrogen was used as the carrier gas.

LED Fabrication and Transfer: To fabricate LED devices, very thin metal layers of Ni/Au (2.5/2.5 nm) were first deposited onto the p-GaN surface of the GaN-based coaxial LED nanostructures, and rapid thermal annealing was performed under ambient air at 500 °C for 2 min to form semitransparent ohmic contacts. To enable current spreading among the nanostructures, additional Ni/Au layers (5/5 nm) were deposited after filling the gaps among the nanostructures with the insulating polymer poly(methyl methacrylate) (PMMA). After LED fabrication and PMMA spin-coating, the entire device structure fabricated on graphene films was released from the 300-nm-thick SiO₂/Si substrate by etching the sacrificial SiO₂ layer using a buffered oxide etchant. Complete release took a few tens of minutes, depending on the sample size. The LEDs on the graphene films released from the supporting substrate were readily transferred on to Cu-coated PET substrate in deionized water (see Supporting Information, Figure S2). At this time, the devices could be adhered to the substrate because of the van der Waals interaction between graphene and Cu.^[22]

Surface Morphology and Crystal Structure Characterization: The morphology and structural characteristics of the GaN-based coaxial LED nanostructure on graphene films were investigated using field-emission scanning electron microscopy (FE-SEM; Carl Zeiss SUPRA 55VP) and high-resolution transmission electron microscopy (HR-TEM; FEI Tecnai G² F30), respectively. For cross-sectional TEM analysis, samples were milled with 30 kV-accelerated gallium ions using a focused ion beam machine (FEI NOVA 200 Nanolab) in dualbeam mode.

Electrical and EL Characterization: The EL and *I–V* characteristics of the devices were measured by applying a DC voltage to the device using a source meter (Keithley 2400). The EL spectra were measured using a monochromator and a detection system equipped with a charge-coupled device.

Acknowledgements

This work was financially supported by the National Creative Research Initiative Project (grant R16-2004-004-01001-0) of the Korea Science and Engineering Foundations (KOSEF). S.-R.J. acknowledges the support by Energy Resource R&D program (No. 20102010100020) under the Ministry of Knowledge Economy, Korea. S.B. and B.H.H. acknowledge the support by the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0028075, 2010-0081966, and 2011-0006268).

> Received: June 24, 2011 Revised: August 2, 2011 Published online: September 8, 2011

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