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2010 Nanotechnology 21 175201

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Large-scale patterned multi-layer graphene films as transparent conducting electrodes for GaN light-emitting diodes

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Received 2 February 2010, in final form 10 March 2010

Published 6 April 2010

Online at stacks.iop.org/Nano/21/175201

Abstract

This work demonstrates a large-scale batch fabrication of GaN light-emitting diodes (LEDs) with patterned multi-layer graphene (MLG) as transparent conducting electrodes. MLG films were synthesized using a chemical vapor deposition (CVD) technique on nickel films and showed typical CVD-synthesized MLG film properties, possessing a sheet resistance of $\sim 620 \Omega/\square$ with a transparency of more than 85% in the 400–800 nm wavelength range. The MLG was applied as the transparent conducting electrodes of GaN-based blue LEDs, and the light output performance was compared to that of conventional GaN LEDs with indium tin oxide electrodes. Our results present a potential development toward future practical application of graphene electrodes in optoelectronic devices.

 Online supplementary data available from stacks.iop.org/Nano/21/175201/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Graphene is anticipated to play a crucial role in future use as a valuable component in electronics and optoelectronics due to its excellent electrical, optical, and mechanical properties [1–6]. Graphene has been prepared by several techniques, including (i) precipitation on a silicon carbide surface [7], (ii) mechanical exfoliation from graphite [1], (iii) reduction of exfoliated graphene oxide [8], and (iv) growth by chemical vapor deposition (CVD) on catalytic metal

surfaces [9–14]. Among these, graphene films grown by CVD on catalytic metal surfaces is especially interesting for the purpose of constructing electrodes, because it has been successfully used to synthesize large-scale, conductive, and transparent graphene films from catalytic reactions that can be transferred onto arbitrary substrates [9, 11]. Optoelectronic devices such as light-emitting diodes (LEDs) have received vast attention from the research and development sector [15, 16]. Indium tin oxide (ITO) is widely used as the transparent conducting electrode for these devices, but ITO is costly, and shows poor transparency in the blue and near-infrared light ranges, instability in the presence of acids or bases, and susceptibility to ion diffusion into the substrate [17, 18]. Therefore, there is a significant need for a novel electrode material that can replace ITO for

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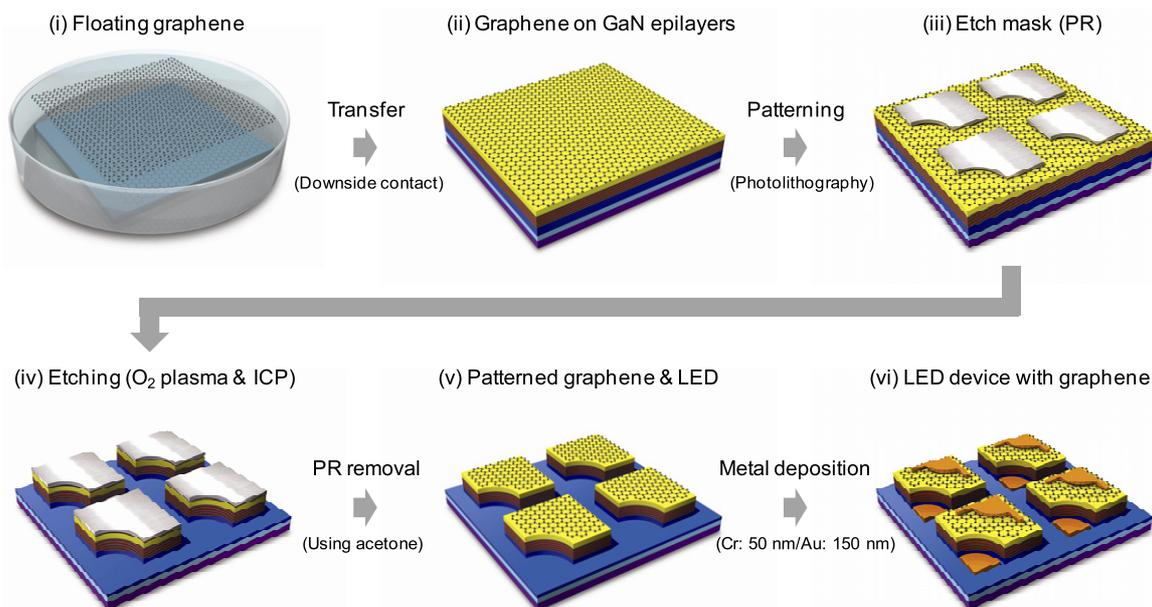


Figure 1. Processes of batch fabrication for GaN-based LEDs with patterned MLG electrodes: (i) a MLG film floats after etching of the Ni substrate with FeCl₃, (ii) the MLG film is transferred onto GaN-based LED epilayers, (iii) patterned PR etch masks are formed by photolithography, (iv) etching of the MLG film and the GaN LED epilayers is performed, (v) the PR is removed, and (vi) metal electrodes are deposited to complete the device fabrication.

application in optoelectronic devices. To this end, graphene-based transparent electrodes have attracted significant attention for their advantages in material properties mentioned above. Several pioneering works have reported the application of graphene-based thin films as transparent electrodes of organic solar cells, liquid crystal displays, and organic LEDs [18–22]. However, most of these researches were not based on a large-scale batch fabrication of multiple devices which is an important development step for more practical applications of graphene-based films.

Our work applies CVD-synthesized multi-layer graphene (MLG) films as transparent electrodes of GaN-based blue LEDs. The MLG films synthesized in our study showed a sheet resistance of $\sim 620 \Omega/\square$ with a transparency of more than 85% in the 400–800 nm wavelength range. Using this transparent MLG electrode, a large-scale simultaneous production of multiple GaN LED devices was demonstrated. The results as regards the electroluminescence (EL) spectra and light output performance showed that the MLG electrode on the GaN LED device successfully operated as a transparent current spreading layer. Therefore, our work of large-scale batch fabrication of LEDs with CVD-synthesized MLG electrodes may promote the application of the graphene-based thin films in optoelectronic devices.

2. Experimental details

The procedure of fabrication of the MLG films began with the evaporation of a 300 nm Ni film on a SiO₂/Si substrate by an e-beam evaporator. Then, the Ni-coated substrates ($2 \times 2 \text{ cm}^2$ or more in size) were loaded into a quartz tube (horizontal-flow CVD reactor) and heated at 300 °C under a flow of Ar (192 sccm) and H₂ (8 sccm) at ambient pressure for 30 min

to eliminate the oxidized layer on the Ni surface. Detailed investigation revealed that this pre-annealing reduced the defect density as well as the amount of oxidized components in the synthesized graphene films (see supporting information, figures S3 and S4, available at stacks.iop.org/Nano/21/175201/mmedia). Then, the CVD growth of MLG films was carried out at 900 °C with a flow of 5 sccm of CH₄ gas and 150 sccm of 4% H₂ in an Ar gas mixture for 5 min. Once the growth was complete, the MLG film was released from the nickel layers on the substrate by etching in an aqueous iron chloride (FeCl₃) solution (1 M) [9]. The MLG films were then transferred to other substrates for analysis and characterization as well as for LED application.

Figure 1 shows the process of fabrication of the LED devices with MLG electrodes. The CVD-grown large-scale MLG film floated on the surface of the solution, separated from the substrate after etching the Ni layers (step (i)). Then, the MLG film was transferred onto the top surface (p-GaN layer) of GaN-based LED epilayers to make the electrical contact (step (ii)). The GaN-based LED epilayers were grown on a *c*-plane (0001) sapphire substrate by metal-organic chemical vapor deposition (MOCVD). After the growth of a 25 nm thick GaN nucleation layer at 550 °C, a 2 μm thick undoped GaN layer and a 2 μm thick n-GaN layer were grown at 1020 °C. Then, five InGaN/GaN multiple quantum wells (MQWs) were grown at 770 °C, and this was followed by the growth of a 200 nm thick p-GaN layer at 950 °C. After transferring the MLG as a transparent current spreading layer, the patterned regions were covered with protective photoresist (PR) as an etch mask (step (iii)). To fabricate the LEDs, MLG films and GaN epilayers were etched by an inductively coupled plasma (ICP) etching process using Cl₂/CH₄/H₂/Ar source gases until the n-GaN layer was exposed for n-type ohmic

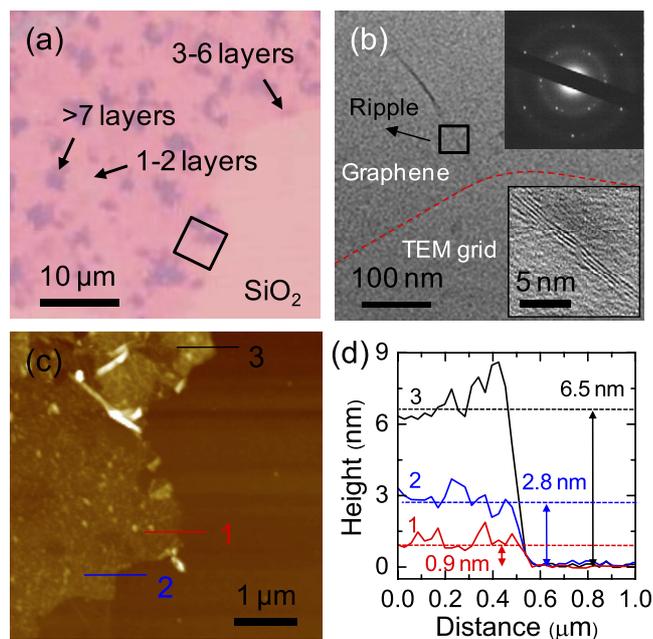


Figure 2. (a) Optical image of a graphene film showing various numbers of layers. (b) TEM image of a graphene bilayer. The insets show the electron diffraction pattern (upper) and a high-resolution TEM image of the rippled region (lower) of a graphene bilayer. (c) AFM image of the boxed area in (a). (d) Topographic height profiles across the lines indicated in (c).

contact (step (iv)). The protective PR was then removed using hot acetone (step (v)). Finally, p- and n-contact pads consisting of Cr (50 nm)/Au (150 nm) were deposited by an electron-beam evaporator (step (vi)). After the device fabrication of the GaN LEDs with MLG electrodes, the electrical and optical characteristics were measured using a semiconductor parameter analyzer (Model B1500A, Agilent, Inc.) and a Si photodiode connected to an optical power meter.

3. Results and discussion

Before applying the CVD-synthesized MLG films to the GaN LEDs, the film properties were investigated. The change of interference color in an optical image (figure 2(a)) of a film deposited on Si substrates with 300 nm SiO₂ layers indicates the film thicknesses [11, 21]. The light pink, pink, and purple regions have roughly 1, 3, and 7 nm thicknesses, as measured by AFM (figures 2(c) and (d)), corresponding to monolayers or bilayers, 5–7 layers, and more than ~17 layers, respectively [23]. Typically, our synthesized MLG films contained 2–10 layers of graphene. Figure 2(b) shows a low-magnification TEM image of a bilayer graphene region containing a ripple, marked by a square in the middle. A high-resolution TEM image of this region (the lower inset of figure 2(b)) shows the number of graphene layers as well as the interlayer distance [9, 11]. The interlayer spacing was found to be 3.45 ± 0.09 Å. In addition, the electron diffraction (ED) pattern on a bilayer graphene film (the upper inset of figure 2(b)) reveals a hexagonal pattern, confirming the threefold symmetry of the arrangement of carbon atoms in graphene. From this ED pattern, the in-plane graphene lattice

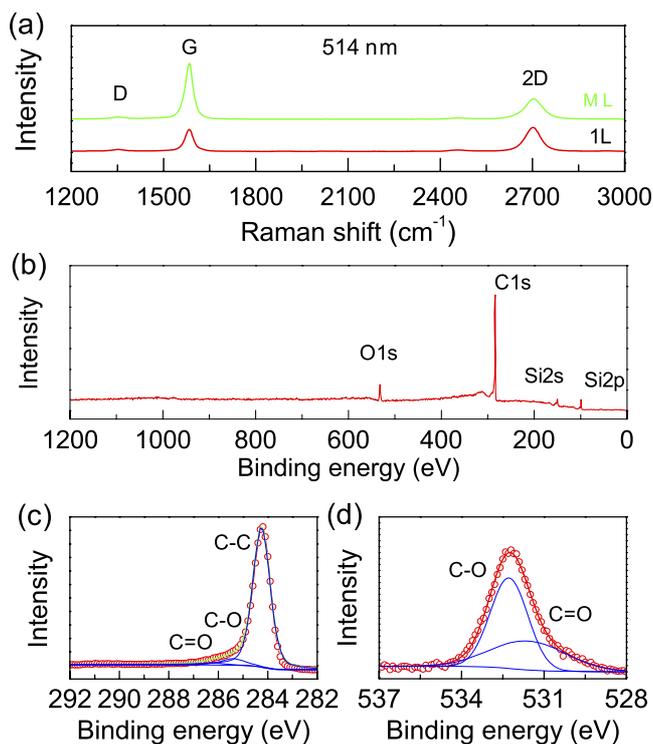


Figure 3. (a) Raman spectra of single (1L) and multi-layer (ML) graphene films in the range of 1200–3000 cm⁻¹. (b) XPS spectrum of a graphene film. XPS spectrum around the C 1s (c) and O 1s (d) peaks. For such analysis, graphene films were transferred to the bare Si substrate after eliminating the native oxide by means of a buffered oxide etch (BOE).

constant was estimated to be 2.44 ± 0.01 Å (see supporting information, figures S1 and S2, available at stacks.iop.org/Nano/21/175201/mmedia).

Raman spectra of our MLG films on SiO₂/Si wafers exhibited typical graphene spectra as shown in figure 3(a). In particular, the observed small D band intensity as compared to the G band intensity indicated low levels of defects or local disorder in our MLG films [24]. X-ray photoelectron spectroscopy (XPS) was also employed to investigate the surface chemical state of the graphene films. The survey XPS spectra depict the full range of binding energy from 0 to 1200 eV (figure 3(b)), indicating that the main chemical components in our samples are C 1s, O 1s, Si 2s, and Si 2p. Excluding the Si peaks that originated from the Si substrate, the constituents of these graphene films are C and O. The C 1s XPS spectrum is split into three functional groups (figure 3(c)), with a small contribution from the oxygenated carbon atoms. The weight percentage of non-oxygenated carbon in this graphene is estimated to be 91% by the analysis of the C 1s and O 1s spectra (figures 3(c) and (d)).

Moreover, to investigate the transparencies of MLG and ITO films, CVD-synthesized MLG sheet was transferred to a glass substrate (the inset of figure 4(a)), and a 150 nm thick ITO film was deposited onto quartz using an e-beam evaporator, this being followed by rapid thermal annealing in air at 500 °C for 1 min. ITO film showed a sheet resistance of ~ 180 Ω/□. Figure 4(a) shows the transmittances of graphene films with different growth times as compared with that for ITO film in

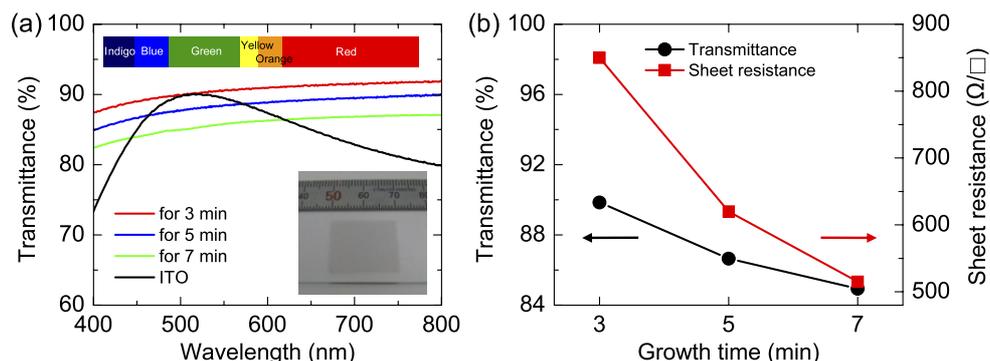


Figure 4. (a) Transmittance characteristics of MLG films with different growth times of 3, 5, and 7 min in comparison to those of an ITO film. The inset shows a photograph of a centimeter-scale MLG film on a glass substrate. (b) Transmittance and sheet resistance of MLG films as a function of the growth time.

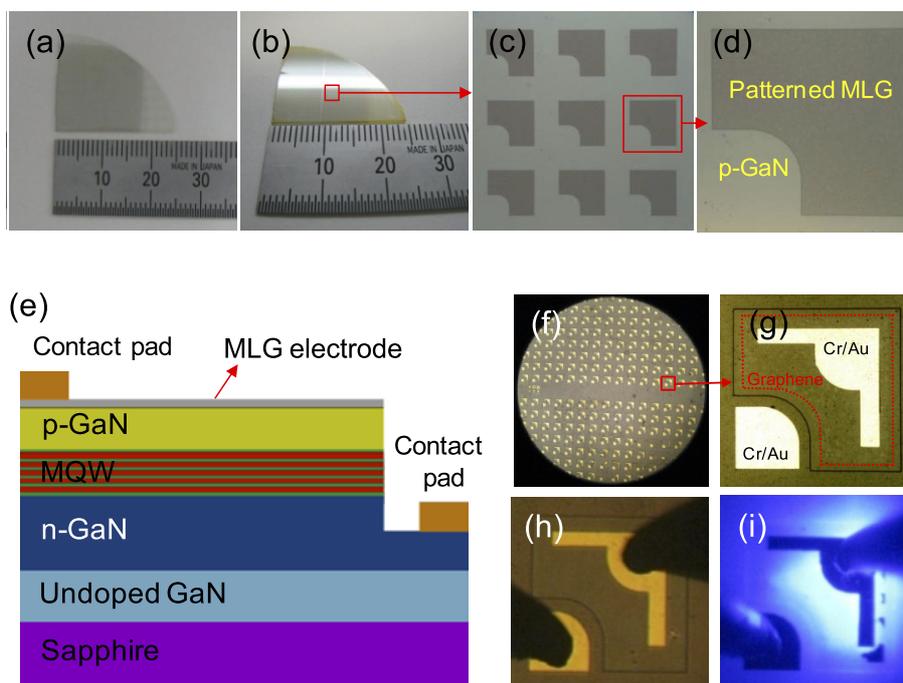


Figure 5. ((a)–(d)) Photographs showing the large-scale fabrication processes for MLG-electrode GaN LEDs. (e) Schematic cross-sectional view of the GaN-based LED structure with a transparent MLG electrode. ((f)–(i)) Optical micrographs of GaN LEDs with transparent MLG electrodes; (f) large-area patterned multiple LED devices and (g) an individual LED. (h) LED with tip probes attached before applying the input current and (i) after applying an input current of 100 μ A.

the visible wavelength range, measured using a UV–visible absorption spectrometer (Lambda 750 UV–Vis Spectrometer, Perkin-Elmer, Inc.). Unlike the ITO film, which only shows good transmittance for wavelengths from 450 to 600 nm, the MLG film maintains good transmittance throughout the entire range of wavelengths. Furthermore, we investigated the transmittances and the sheet resistances of the MLG films synthesized at different growth times as summarized in figure 4(b). The sheet resistances were measured by the van der Pauw four-probe method using a Hall measurement system [25]. The transmittance (at 450 nm wavelength) and sheet resistance of the three different MLG films (growth time = 3, 5, and 7 min) were found to be 90% and $\sim 850 \Omega/\square$, 87% and $\sim 620 \Omega/\square$, 85% and $\sim 520 \Omega/\square$, respectively. Our film qualities are comparable to the results reported by Kim *et al*

and Reina *et al* [9, 11]. Thus, these observed properties reveal the merits of MLG films as transparent electrodes for optical electronic devices operating over a wide range of wavelengths.

In this regard, the CVD-synthesized MLG film was applied as a transparent electrode for GaN-based LEDs. The LEDs with MLG electrodes were fabricated with the procedure described in section 2. Figures 5(a)–(d) show photographs displaying the large-scale fabrication processes for MLG-electrode LEDs. A $2 \times 2 \text{ cm}^2$ MLG sheet was transferred to a quarter of a two-inch GaN epilayer (figure 5(a)) by the following processes [9]: (i) a CVD-synthesized graphene film was separated from the Ni catalytic layer after etching the Ni layer in 1 M FeCl_3 aqueous solution, (ii) the floating graphene film was transferred to DI water by the scooping-up technique in order to wash out the etchant, and (iii) the graphene film

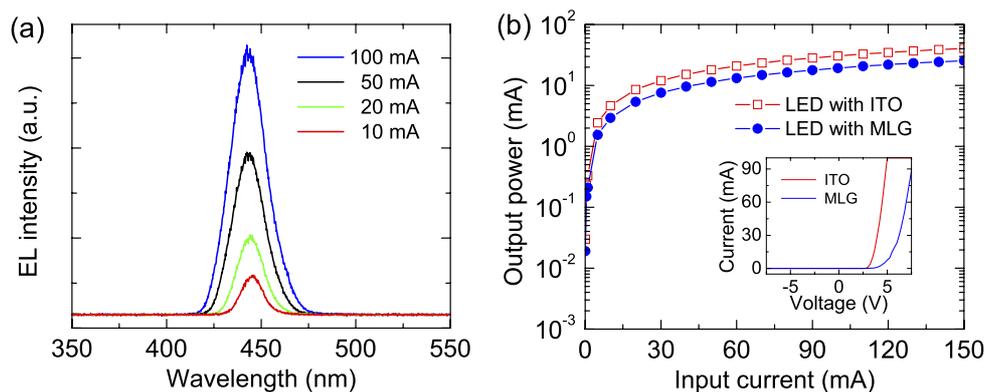


Figure 6. (a) EL spectra of a GaN LED with transparent MLG electrodes at input currents of 10, 20, 50, and 100 mA. (b) Light output powers of a GaN LED with MLG electrodes (blue filled circles) and ITO electrodes (red open squares) as a function of input current. The inset shows current–voltage (I – V) characteristics of the GaN LEDs with MLG (blue curve) and ITO (red curve) electrodes.

floating on DI water can be transferred to the GaN epilayer by the same technique. Then, after patterning of the sample by photolithography (figure 5(b)), the graphene film and GaN epilayers were etched until the n-GaN layer was exposed. Zoomed-in pictures (figures 5(c) and (d)) show patterned MLG electrodes. The schematic cross-sectional view of our MLG-electrode LED is illustrated in figure 5(e). The structure shows the MLG anode, the active luminescent layer (p-GaN/MQW/n-GaN), the Cr/Au cathode, undoped GaN, and the sapphire substrate. The optical micrographs of the fabricated LEDs are shown in figures 5(f) and (g). They present large-scale batch-process-fabricated multiple devices with patterned MLG electrodes and a single device among them, respectively. Figures 5(h) and (i) show optical micrographs of a MLG-electrode LED before and after applying an input current, respectively. Blue light emission was clearly visible even at a low input current of 100 μ A.

Figure 6(a) presents the EL spectra of fabricated MLG-electrode GaN-based blue LEDs at input currents of 10, 20, 50, and 100 mA. As the input current varied from 10 to 100 mA, the EL intensity increased and the EL peak position of the LED was blue-shifted from 445 to 443 nm. The shift of the EL peaks towards higher energy is due to the combined effects of the band-filling phenomena of the localized energy states formed by potential fluctuations in the MQWs and the screening effect of the polarization-induced electric field produced by carriers [26, 27]. Also, the brightness variation of the light emission from the MLG-electrode LED was clearly observed at a wide range of input currents (see supporting information, figure S5, available at stacks.iop.org/Nano/21/175201/mmedia), indicating that the MLG electrode successfully operated as a transparent current spreading layer over this current range. Figure 6(b) shows the light output power versus input current characteristics of the LEDs fabricated with MLG electrodes (blue filled circles) and those made with ITO (red open squares). The output power of MLG-electrode GaN LEDs continuously grew with increase in input current up to 150 mA. At input currents below 10 mA, the output power of the MLG-electrode LEDs is comparable to that of the ITO-electrode LEDs. However, at input currents above 10 mA, the output power of the MLG-electrode LEDs

was less than that of the ITO-electrode LEDs, because the higher contact and sheet resistance of the MLG electrode as compared to that of the ITO electrode yielded a larger voltage drop (or more power loss) across the contact and the MLG electrode [22]. The output power of the MLG-electrode LED was about 63% of that with the ITO-electrode LED at an input current of 20 mA. The inset of figure 6(b) compares the current–voltage (I – V) characteristics of the GaN LEDs with MLG and ITO electrodes. The forward voltages (defined at an input current of 20 mA) were found to be \sim 5.6 V and \sim 3.8 V for the LED with MLG and ITO electrodes, respectively. Further engineering of the MLG film characteristics such as doping to increase the conductivity and tuning of the work function to improve the interface matching between graphene and p-GaN may enhance the device performance of MLG-electrode LEDs. We believe that such improvements of MLG film qualities will be interesting subjects for future research for the practical applications of MLG films as transparent electrodes of optoelectronic devices.

4. Conclusions

In conclusion, this work applied CVD-synthesized multi-layer graphene films as transparent electrodes of GaN-based blue LEDs. The results as regards the EL spectra and light output performance showed that the MLG electrodes on the GaN LED devices successfully operated as a transparent current spreading layer. In particular, we performed a large-scale batch fabrication of multiple LEDs with patterned graphene electrodes. This work demonstrates the possibility of using CVD-synthesized multi-layer graphene film as a potential substitute for ITO films in inorganic LEDs and may promote practical applications of graphene-based thin films as transparent electrodes of many kinds of optoelectronic devices.

Acknowledgments

This work was supported by the Proton Accelerator User Program of Korea, the National Research Laboratory Program, a National Core Research Center grant, the World Class

University Program of the Korean Ministry of Education, Science and Technology, and the Program for Integrated Molecular System at GIST. The authors thank Yun Chang Park at the National Nanofab Center for his assistance in operating the TEM.

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