Near-ultraviolet light-emitting diodes with transparent conducting layer of gold-doped multi-layer graphene

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We report on gold (Au)-doped multi-layer graphene (MLG), which can be used as a transparent conducting layer in near-ultraviolet light-emitting diodes (NUV-LEDs). The optical output power of NUV-LEDs with thermally annealed Au-doped MLG was increased by 34% compared with that of NUV-LEDs with a bare MLG. This result is attributed to the reduced sheet resistance and the enhanced current injection efficiency of NUV-LEDs by the thermally annealed Au-doped MLG film, which shows high transmittance in NUV and UV regions and good adhesion of Au-doped MLG on *p*-GaN layer of NUV-LEDs. © *2013 American Institute of Physics*.
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I. INTRODUCTION

Group III-nitride based light-emitting diodes (LEDs) have been rapidly developed for various applications, such as full-color displays, automobile headlights, traffic lights, and solid-state lighting. Especially, GaN-based ultraviolet (UV) LEDs have attracted much attention for application to fluorescence-based chemical sensing, flame detection, and high density optical data storage. Furthermore, the UV-LED, which pumps red-green-blue phosphors to generate white light, is one of the most promising candidates for solid-state lighting.[1] However, the efficiency of UV-LEDs needs to be further improved to realize solid-state lighting and other applications. It has been reported that the indium composition in the InGaN active layer is much lower in UV-LEDs compared to blue-LEDs and the defects in the InGaN active layer in UV-LEDs act as nonradiative recombination centers due to a lack of indium rich regions acting as the localized recombination sites, resulting in a lower efficiency of UV-LEDs.[2] Moreover, it is necessary to increase the transmittance of *p*-contact layer, since photons generated in the active region of UV-LEDs are partially absorbed in the *p*-contact layer. Although indium tin oxide (ITO) is widely used as a transparent conducting layer (TCL) in optoelectronic devices, the transmittance of ITO decreases rapidly in the UV and near UV (NUV) regions.[3] Therefore, it is necessary to find a suitable material for TCLs that have high transmittance in the UV region as well as high electrical conductivity. Recently, graphene has been extensively studied as a promising material to replace ITO because graphene has very high carrier mobility and conductivity.[4,5] In particular, the transmittance of graphene in the NUV and UV region is much higher than that of ITO.[6] The work function of graphene is also very close to that of ITO and the sheet resistance of multi-layer graphene (MLG) can be controlled by changing the number of graphene layers. Many research groups have investigated the characteristics of graphene-based thin films for use as TCLs in optoelectronic devices.[7–11] However, the use of bare MLG as a TCL in GaN-based LEDs has intrinsic limitations for current injection due to the difference of work function between MLG and *p*-GaN layer and high sheet resistance of bare MLG.[7,8] To increase the current injection to GaN-based blue LEDs, the work function of MLG and the current-voltage (*I-V*) characteristics were investigated by doping the MLG with aqueous gold chloride ($AuCl_3$) solution.[12] Our group also reported the NUV-LEDs with Au-doped MLG by using aqueous $AuCl_3$ solution.[13] However, the MLG film was easily detached from the *p*-GaN layer during the formation of *p*-pad metal electrode on the graphene due to the weak adhesion between MLG film and *p*-GaN layer. The poor adhesion resulted in a low current injection into NUV-LEDs.[13] In this letter, we studied the Au-doped MLG films as a TCL in NUV-LEDs with an emission wavelength of 415 nm. Instead of using aqueous Au solutions to dope the MLG films, the Au films were deposited on the MLG film and thermally annealed to improve the electrical and optical properties of MLG films. This reduced the sheet resistance of MLG and improved the current spreading, transmittance of MLG in the NUV and UV region, and adhesion of MLG film on *p*-GaN layer, resulting in the increase of optical output power of NUV-LEDs by 34% at 20 mA.

II. EXPERIMENTAL DETAILS

MLG films were grown by chemical vapor deposition (CVD) method. To synthesize a MLG film, a 300 nm-thick Ni layer was deposited on a SiO_2/Si substrate, and then transferred into a CVD chamber. The CVD growth of a MLG film was performed at 900 °C under a flow of CH_4 gas and H_2 in

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an Ar gas mixture. The substrate was then rapidly cooled to room temperature to suppress excessive precipitation of carbon atoms. Finally, the MLG film was released from the Ni layer on the substrate by etching in aqueous iron chloride ($FeCl_3$) solution. After removing the Ni layer, the floating MLG films were directly transferred onto NUV-LEDs. Figures 1(a) and 1(b) show the schematic diagrams of NUV-LEDs with MLG and Au-doped MLG as TCLs, respectively. The LEDs with an NUV emission at 415 nm were grown using metalorganic chemical vapor deposition (MOCVD) on a *c*-plane (0001) sapphire substrate. 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, multiple quantum wells (MQWs) consisting of five periods of undoped InGaN wells and GaN barriers were grown at 800 °C, followed by the growth of a 200 nm-thick *p*-GaN layer at 980 °C. To fabricate LEDs, a *p*-GaN layer was etched by inductively coupled plasma (ICP) etching process until the *n*-GaN layer was exposed for an *n*-type ohmic contact. After transferring the MLG film onto the *p*-GaN layer, the MLG film in the *p*- and *n*-pad electrode regions was selectively removed by photolithography and reactive ion etching process. To investigate the influence of Au-doped MLG film on the electrical and optical properties of NUV-LEDs, NUV-LEDs with Au-doped MLG as a TCL were also fabricated. To produce an Au-doped MLG, a 0.2 nm-thick Au layer was deposited on a MLG film by electron-beam evaporation, and then thermally annealed at 700 °C for 5 min under nitrogen ambient in a rapid thermal annealing (RTA) chamber. This was followed by the deposition of Cr/Au on the *n*-GaN layer as an *n*-pad electrode and on the *p*-GaN layer as a *p*-pad electrode. Previously, the MLG film was easily detached from the LED during the lift-off process for metal *p*-pad electrode on the MLG film due to the weak adhesion between MLG film and LED epilayer, showing a poor current-voltage characteristics of LEDs.[13] However, Au-doping method using the metal deposition and thermal annealing improved the adhesion between MLG film and LED epilayer and ohmic contact to *p*-GaN layer, presumably due to the formation of Au nanoparticles and Au diffusion into *p*-GaN layer.[14,15] Furthermore, thermal annealing can remove the oxidized *p*-GaN and residual chemicals on the *p*-GaN surface for good adhesion between MLG film and LED. Figures 1(c) and 1(d) show plan-view scanning electron microscopy (SEM) images of MLG and Au-doped MLG transferred to the top of *p*-GaN layers, respectively. The insets in Figs. 1(c) and 1(d) show optical microscopy images of NUV-LEDs with MLG and Au-doped MLG TCLs, respectively. As shown in Figs. 1(c) and 1(d), the MLG films are well attached on top of *p*-GaN layer without any degradation of MLG film.

III. RESULTS AND DISCUSSIONS

Figures 2(a)–2(c) show atomic force microscopy (AFM) images of MLG, Au-deposited MLG, and Au-doped MLG transferred onto the *p*-GaN layers. AFM image shows that the surface of the MLG film is flat and there are ripple boundary structures on MLG. As shown in Fig. 2(b), the surface of an as-deposited 0.2 nm-thick Au layer on MLG is very similar to that observed in Fig. 2(a). However, the thin Au layer is transformed into Au nanoparticles by thermal annealing via the Ostwald ripening process, as shown in Fig. 2(c).[16,17] The average diameter and height of the Au nanoparticles on the MLG layer are 50 ± 20 nm and 8 ± 5 nm, respectively. For the TCL application in NUV-LEDs, the optical properties of MLG, Au-deposited MLG, and Au-doped MLG on glass wafers were measured by UV-visible spectrometer. As shown in Fig. 2(d), the optical transmittance of MLG at 415 nm, which is the emission wavelength of the NUV-LED used in this study, is 88%. When an Au layer is deposited on MLG, the transmittance of the Au-deposited

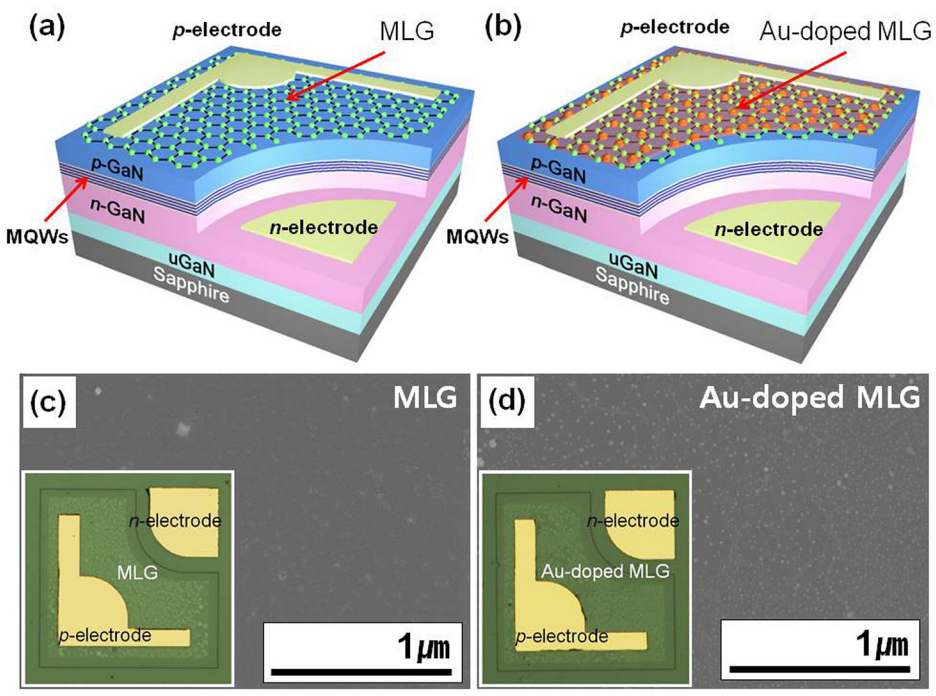

FIG. 1. Schematic diagrams of NUV-LEDs with (a) MLG and (b) Au-doped MLG TCLs. (c) and (d) SEM images of MLG and Au-doped MLG. The inset shows optical microscopy images of NUV-LEDs with MLG and Au-doped MLG TCLs.

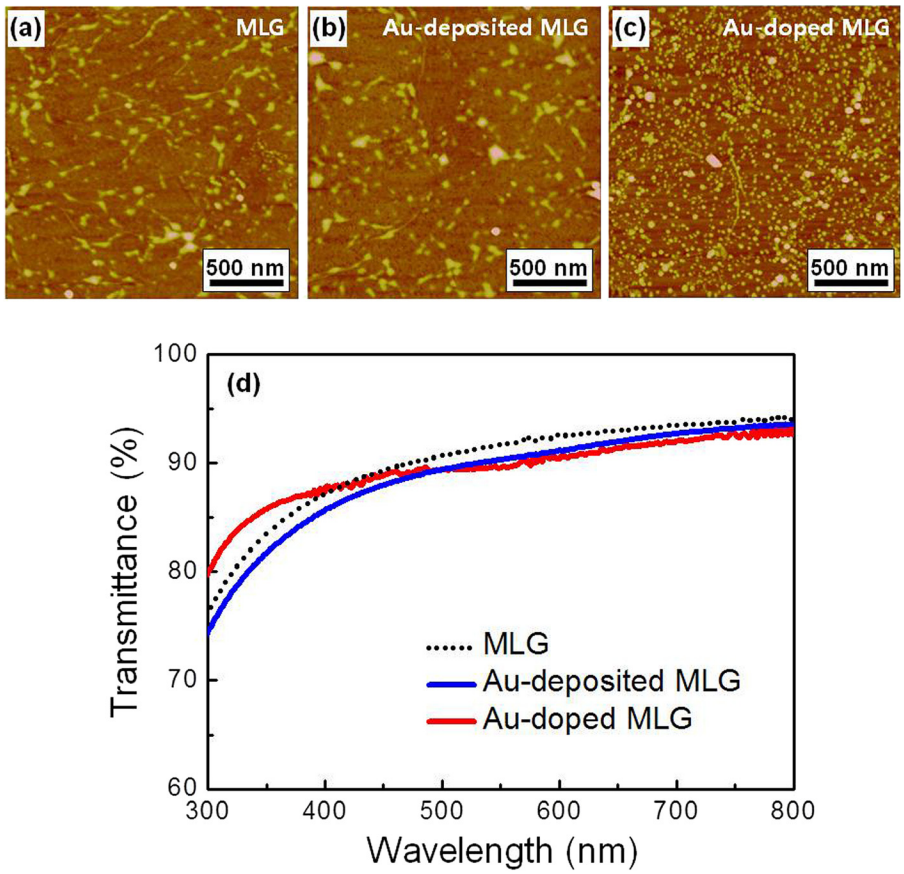

FIG. 2. (a)-(c) AFM images of MLG, Au-deposited MLG, and Au-doped MLG on a *p*-GaN layer. (d) Optical transmittance spectra of MLG, Au-deposited MLG, and Au-doped MLG on glass wafers.

MLG is slightly reduced. However, the transmittance of the Au-deposited MLG is recovered when the Au nanoparticles are formed on MLG after the thermal annealing process. The transmittance of Au-doped MLG is 88% at 415 nm, which is the same as that of the bare MLG film. This value is higher than the transmittance of 80% of a 200 nm-thick ITO film in the same wavelength region.[7] Figure 2(d) also shows that the transmittance of Au-doped MLG is much increased in the UV region compared to that of the bare MLG film, indicating that the Au-doped MLG can be also used in the UV LEDs.

Figure 3 shows normalized Raman spectra of MLG and Au-doped MLG layers deposited on glass wafers. The Raman spectrum of the MLG films exhibits the typical characteristic peaks of graphene films as shown in Fig. 3(a).[18,19] The most dominant peaks in the Raman spectra of the MLG films are the G band at 1580 cm^{-1} and 2D band at 2695 cm^{-1}. Previous studies have revealed that the intensity of the D band is related to basal plane disorder and the weak intensity of the D band compared with that of the G band indicates a low level of defects or local disorder in the MLG films.[18] Furthermore, the ratio of the intensities of the G and 2D bands shows multi-layer type graphene features.[19] The Raman peaks of Au-deposited MLG are similar to those of the MLG film. However, the disorder-induced D band (1350 cm^{-1}), which has been frequently observed in sp^2-bonded carbon-based materials,[9] is slightly increased after deposition of an Au film. The increased D band in the Au-deposited MLG indicates the formation of disorder or defects, which are induced by the Au atoms incorporated in the graphene film.[18–20] However, the intensity of the D band is significantly reduced after thermal annealing of the Au-deposited MLG. Furthermore, the 2D band of the Au-doped

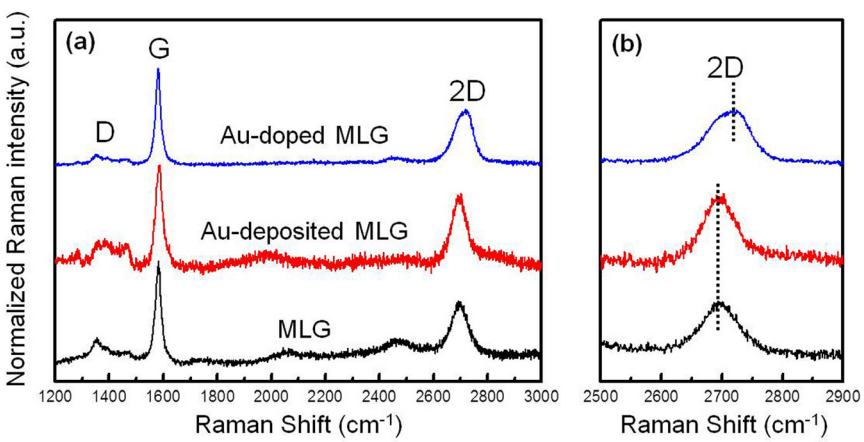

FIG. 3. (a) and (b) Raman spectra of MLG, Au-deposited MLG, and Au-doped MLG on glass wafers.

MLG is broadened and up-shifted compared with those of the MLG and Au-deposited MLG as shown in Fig. 3(b). These results indicate that the Au atoms are diffused in the MLG film by thermal annealing and the diffused Au atoms replace carbon atoms or occupy single and multiple vacancies in the MLG, producing Au-doped MLG.[19–21]

In order to investigate the electrical properties of NUV-LEDs, the *I-V* characteristics were measured. Figure 4 shows the *I-V* curves of NUV-LEDs with MLG and Au-doped MLG TCLs, respectively. As shown in Fig. 4, both NUV-LEDs show rectifying behavior without showing a reverse bias leakage current. The forward voltage of the NUV-LED with an Au-doped MLG TCL is 6.8 V at 20 mA and this is smaller than 7.8 V for the NUV-LED with a MLG TCL. The series resistance of the NUV-LED with an Au-doped MLG TCL is also much decreased compared to that with a MLG TCL. The sheet resistances of MLG were much reduced from 1000 ± 100 Ω/□ to 18 ± 2 Ω/□ by the deposition of Au films and a subsequent annealing process, compared to that of MLG treated by the aqueous $AuCl_3$ solution process.[12,13] Therefore, the improved *I-V* characteristics of the NUV-LEDs with an Au-doped MLG layer can be attributed to the reduced sheet resistance of the Au-doped MLG films and the decreased contact resistance between Au-doped MLG and *p*-GaN layer.

Figure 5(a) shows electroluminescence (EL) spectra of NUV-LEDs with MLG and Au-doped MLG TCLs at injection currents of 1 and 10 mA, respectively. The EL intensities of NUV-LEDs with an Au-doped MLG TCL are much higher than those of NUV-LEDs with a bare MLG TCL. This result is attributed to the improved current injection efficiency of NUV-LEDs with Au-doped MLG TCL as shown in Fig. 4. The inset of Fig. 5(a) shows EL emission from NUV-LEDs with MLG and Au-doped MLG TCLs at 10 mA. The NUV emission through the Au-doped MLG TCL is more uniform and stronger than that from NUV-LEDs with a bare MLG TCL, and this also indicates effective current injection and current spreading in NUV-LEDs having an Au-doped MLG TCL. Figure 5(a) also shows that the EL emission wavelength is slightly blue-shifted from 415 nm at 1 mA to 413 nm at

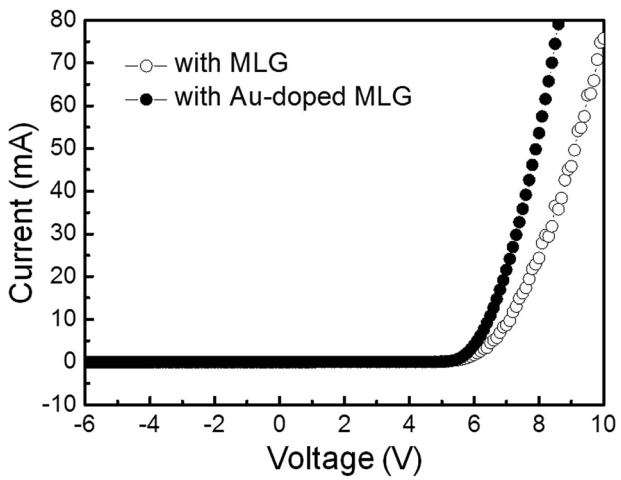

FIG. 4. *I-V* characteristics of NUV-LEDs with MLG and Au-doped MLG TCLs.

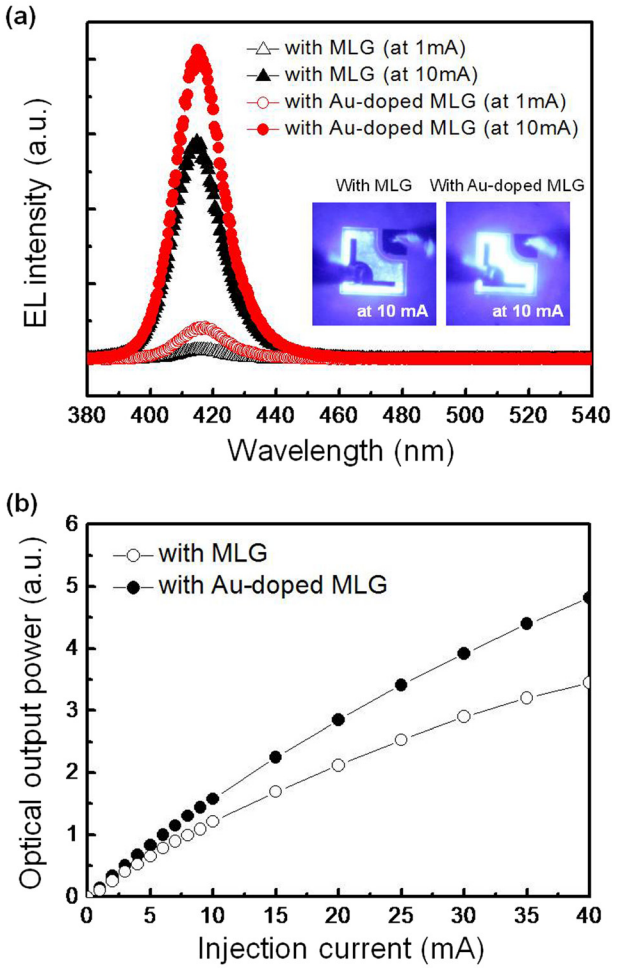

FIG. 5. (a) Room temperature EL spectra of NUV-LEDs with MLG and Au-doped MLG TCLs, which were measured at 1 and 10 mA. The inset shows photographs of NUV-LEDs with MLG and Au-doped MLG TCLs at 10 mA. (b) The optical output power of NUV-LEDs with MLG and Au-doped MLG TCLs.

10 mA. This increase in emission energy with increasing injection current is caused by a screening effect of the polarization-induced electric field by carriers and a band-filling effect of localized energy states formed by potential fluctuation in MQWs.[22] Figure 5(b) shows the optical output power of NUV-LEDs with MLG and Au-doped MLG TCLs as a function of injection current. As shown in Fig. 5(b), the optical output power of NUV-LEDs with an Au-doped MLG TCL is increased by 34% at 20 mA compared with that of NUV-LEDs with a bare MLG TCL. This improvement of the optical output power of NUV-LEDs is attributed to the increased current injection efficiency, current spreading, and transmittance of Au-doped MLG TCL.

IV. CONCLUSIONS

In conclusion, the effect of Au-doping on the transmittance and conductivity of MLG films was studied and the Au-doped MLG was used as a TCL in NUV-LEDs. Au-doped MLG was prepared by the deposition of Au films on MLG and a thermal annealing process. An NUV-LED with a thermally annealed Au-doped MLG showed the low sheet resistance and high current injection in the NUV-LED. The

thermally annealed Au-doped MLG also showed a high transmittance in the NUV and UV regions. The optical output power of NUV-LEDs with a thermally annealed Au-doped MLG TCL was increased by 34% at 20 mA compared to that of NUV-LEDs with a bare MLG TCL.

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