GaN-based light-emitting diodes with graphene/indium tin oxide transparent layer

Wei-Chih Lai,[1,4,*] Chih-Nan Lin,[1] Yi-Chun Lai,[2] Peichen Yu,[2] Gou Chung Chi,[2] and Shoou-Jinn Chang[3,4]

[1]*Department of Photonics, National Cheng Kung University, Tainan 70101, Taiwan*
[2]*Department of Photonics & Institute of Electro-Optical Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan*
[3]*Institute of Microelectronics & Department of Electrical Engineering, National Cheng Kung University, Tainan City 701, Taiwan*
[4]*Institute of Microelectronics & Department of Electrical Engineering, Advanced Optoelectronic Technology Center, Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan 70101, Taiwan*
[*]*weilai@mail.ncku.edu.tw*

Abstract: We have demonstrated a gallium nitride (GaN)-based green light-emitting diode (LED) with graphene/indium tin oxide (ITO) transparent contact. The ohmic characteristic of the p-GaN and graphene/ITO contact could be preformed by annealing at 500 °C for 5 min. The specific contact resistance of p-GaN/graphene/ITO (3.72E-3 $\Omega\cdot cm^2$) is one order less than that of p-GaN/ITO. In addition, the 20-mA forward voltage of LEDs with graphene/ITO transparent (3.05 V) is 0.09 V lower than that of ITO LEDs (3.14 V). Besides, We have got an output power enhancement of 11% on LEDs with graphene/ITO transparent contact.

OCIS codes: (230.3670) Light-emitting diodes; (250.0250) Optoelectronics.

References and links

1. T. Mukai, M. Yamada, and S. Nakamura, "Characteristics of InGaN-based UV/blue/green/amber/red light-emitting diodes," Jpn. J. Appl. Phys. **38**(7A), 3976–3981 (1999).
2. T. Mukai, M. Yamada, and S. Nakamura, "Current and temperature dependences of electroluminescence of InGaN-based UV/blue/green light-emitting diodes," Jpn. J. Appl. Phys. Lett. **37**(11B), L1358–L1361 (1998).
3. T. Fujii, Y. Gao, R. Sharma, E. L. Hu, S. P. DenBaars, and S. Nakamura, "Increase in the extraction efficiency of GaN-based light-emitting diodes via surface roughening," Appl. Phys. Lett. **84**(6), 855–857 (2004).
4. S. I. Na, G. Y. Ha, D. S. Han, S. S. Kim, J. Y. Kim, J. H. Lim, D. J. Kim, K. I. Min, and S. J. Park, "Selective wet etching of p-GaN for efficient GaN-based light-emitting diodes," IEEE Photonics Technol. Lett. **18**(14), 1512–1514 (2006).
5. C. H. Kuo, C. C. Lin, S. J. Chang, Y. P. Hsu, J. M. Tsai, W. C. Lai, and P. T. Wang, "Nitride-based light-emitting diodes with p-AlInGaN surface layers," IEEE Electron. Device Lett. **52**(10), 2346–2349 (2005).
6. S. J. Chang, C. S. Chang, Y. K. Su, R. W. Chuang, W. C. Lai, C. H. Kuo, Y. P. Hsu, Y. C. Lin, S. C. Shei, H. M. Lo, J. C. Ke, and J. K. Sheu, "Nitride-based LEDs with an SPS tunneling contact Layer and an ITO transparent contact," IEEE Photonics Technol. Lett. **16**(4), 1002–1004 (2004).
7. P. H. Chen, W. C. Lai, L. C. Peng, C. H. Kuo, C. L. Yeh, J. K. Sheu, and C. J. Tun, "GaN-based LEDs with AZO: Y upper contact," IEEE Trans. Electron. Dev. **57**(1), 134–139 (2010).
8. C. H. Kuo, S. J. Chang, Y. K. Su, R. W. Chuang, C. S. Chang, L. W. Wu, W. C. Lai, J. F. Chen, J. K. Sheu, H. M. Lo, and J. M. Tsai, "Nitride-based near-ultraviolet LEDs with an ITO transparent contact," Mater. Sci. Eng. B **106**(1), 69–72 (2004).
9. C. J. Tun, J. K. Sheu, B. J. Pong, M. L. Lee, M. Y. Lee, C. K. Hsieh, C. C. Hu, and G. C. Chi, "Enhanced light output of GaN-based power LEDs with transparent Al-doped ZnO current spreading layer," IEEE Photon. Technol. Lett. **18**(1), 274–276 (2006).
10. X. Wang, L. Zhi, and K. Müllen, "Transparent, conductive graphene electrodes for dye-sensitized solar cells," Nano Lett. **8**(1), 323–327 (2008).
11. S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, and S. Iijima, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," Nat. Nanotechnol. **5**(8), 574–578 (2010).
12. H. Bi, F. Huang, J. Liang, X. Xie, and M. Jiang, "Transparent conductive graphene films synthesized by ambient pressure chemical vapor deposition used as the front electrode of CdTe solar cells," Adv. Mater. **23**(28), 3202–3206 (2011).

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13. S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, and S. Iijima, "Roll-to-roll production of 30-inch graphene films for transparent electrodes," Nat. Nanotechnol. **5**(8), 574–578 (2010).
14. H. Bi, F. Huang, J. Liang, X. Xie, and M. Jiang, "Transparent conductive graphene films synthesized by ambient pressure chemical vapor deposition used as the front electrode of CdTe solar cells," Adv. Mater. **23**(28), 3202–3206 (2011).
15. Y. Wang, S. W. Tong, X. F. Xu, B. Ozyilmaz, and K. P. Loh, "Interface engineering of layer-by-layer stacked graphene anodes for high-performance organic solar cells," Adv. Mater. **23**(13), 1514–1518 (2011).
16. J. M. Lee, J. W. Choung, J. Yi, D. H. Lee, M. Samal, D. K. Yi, C.-H. Lee, G.-C. Yi, U. Paik, J. A. Rogers, and W. I. Park, "Vertical pillar-superlattice array and graphene hybrid light emitting diodes," Nano Lett. **10**(8), 2783–2788 (2010).
17. G. Jo, M. Choe, C.-Y. Cho, J. H. Kim, W. Park, S. Lee, W.-K. Hong, T.-W. Kim, S.-J. Park, B. H. Hong, Y. H. Kahng, and T. Lee, "Large-scale patterned multi-layer graphene films as transparent conducting electrodes for GaN light-emitting diodes," Nanotechnology **21**(17), 175201 (2010).
18. T. H. Seo, T. S. Oh, S. J. Chae, A. H. Park, K. J. Lee, Y. H. Lee, and E. K. Suh, "Enhanced light output power of GaN light-emitting diodes with graphene film as a transparent conducting electrode," Jpn. J. Appl. Phys. **50**, 125103 (2011).
19. B.-J. Kim, G. Yang, H.-Y. Kim, K. H. Baik, M. A. Mastro, J. K. Hite, C. R. Eddy, F. Ren, S. J. Pearton, and J. Kim, "GaN-based ultraviolet light-emitting diodes with $AuCl_3$-doped graphene electrodes," Opt. Express **21**(23), 29025–29030 (2013).
20. J. M. Lee, H. Y. Jeong, K. J. Choi, and W. I. Park, "Metal/graphene sheets as p-type transparent conducting electrodes in GaN light emitting diodes," Appl. Phys. Lett. **99**(4), 041115 (2011).
21. T. H. Seo, K. J. Lee, T. S. Oh, Y. S. Lee, H. Jeong, A. H. Park, H. Kim, Y. R. Choi, E. K. Suh, T. V. Cuong, V. H. Pham, J. S. Chung, and E. J. Kim, "Graphene network on indium tin oxide nanodot nodes for transparent and current spreading electrode in InGaN/GaN light emitting diode," Appl. Phys. Lett. **98**(25), 251114 (2011).
22. M. Choe, C. Y. Cho, J. P. Shim, W. Park, S. K. Lim, W. K. Hong, B. H. Lee, D. S. Lee, S. J. Park, and T. Lee, "Au nanoparticle-decorated graphene electrodes for GaN-based optoelectronic devices," Appl. Phys. Lett. **101**(3), 031115 (2012).
23. B.-J. Kim, C. Lee, M. A. Mastro, J. K. Hite, C. R. Eddy, F. Ren, S. J. Pearton, and J. Kim, "Buried graphene electrodes on GaN-based ultra-violet light-emitting diodes," Appl. Phys. Lett. **101**(3), 031108 (2012).
24. C. H. Kuo, C. C. Lin, S. J. Chang, Y. P. Hsu, J. M. Tsai, W. C. Lai, and P. T. Wang, "Nitride-based light-emitting diodes with p-AlInGaN surface layers," IEEE Electron. Dev. **52**(10), 2346–2349 (2005).
25. C. H. Kuo, S. J. Chang, Y. K. Su, R. W. Chuang, C. S. Chang, L. W. Wu, W. C. Lai, J. F. Chen, J. K. Sheu, H. M. Lo, and J. M. Tsai, "Nitride-based near-ultraviolet LEDs with an ITO transparent contact," Mater. Sci. Eng. B **106**(1), 69–72 (2004).
26. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, "Electric field effect in atomically thin carbon films," Science **306**(5696), 666–669 (2004).
27. F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, "Graphene photonics and optoelectronics," Nat. Photonics **4**(9), 611–622 (2010).

1. Introduction

Nitride-based materials have recently emerged as important semiconductor materials and has led to the development of high-performance light emitters from ultraviolet (UV) to blue and green spectral regions [1,2]. For example, gallium nitride (GaN)-based blue and green light-emitting diodes (LEDs) have already been extensively used in full-color displays and as high-efficiency light sources for traffic light lamps. High efficiency nitride-based LEDs are also potentially useful for solid-state lighting. To achieve solid-state lighting, however, the output efficiency of these LEDs should be enhanced further. Several methods have been used to improve the output efficiency of GaN-based LEDs by enhancing light extraction efficiency, such as textured surfaces [3–5], a highly transparent p-contact layer [6,7], a proper substrate design [8], and flip chip packaging [9]. Thus far, indium tin oxide (ITO) works very well with conventional III-nitride GaN-based LEDs for the transparent contact. However, alternative transparent electrodes with optical and electrical performances similar to or better than those of ITO materials without drawbacks in the UV wavelength region are still needed. Additional issues associated with the use of ITO include the high prices of indium and its susceptibility to diffusion into the semiconductor, sensitivity to acids and bases during device processing, and mechanical brittleness [10]. Graphene, a single-atom-thick layer of sp2-hybridized carbon atoms, offers exceptional characteristics such as high transparency, low sheet resistance (R_s), suppleness, and so on [11,12]. Recent demonstrations of large-scale growth and a facile transfer to arbitrary substrates have enabled the use of graphene as a next-generation transparent conductive electrode in place of ITO for applications such as display devices, solar cells, and LEDs [13–17]. Recently, Jo et al. and Soe et al [17,18]. demonstrated GaN-

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based LEDs with single-layer or multilayer graphene electrode. Nevertheless, the observed forward voltage (V_f) of the device was high (5.6 V at an input current of 20 mA) compared with 3.8 V that is typically reported for ITO-based devices. Kim et al. [19] has reported the V_f reduction of the GaN based UV LEDs with graphene transparent contact by doping $AuCl_3$ in graphene. Besides, an intermediate layer, such as thin metal, nanosized metal, or ITO, is inserted in between graphene and p-GaN to reduce contact resistance [20–22]. Reports have indicated that the V_f of GaN-based LEDs with an intermediate contact layer between graphene and p-GaN can be reduced to as low as that of GaN-based LEDs with ITO only. Moreover, Kim et al. [23] has found that the garphene transparent electrode of GaN based LEDs is highly violable in O_2 ambient during the operation if without proper protection. They introduced a SiNx layer for protection the graphene transparent electrode. In our study, we analyzed GaN-based LEDs with a graphene intermediate layer inserted between ITO and p-GaN. The contact characteristics of p-GaN/graphene/ITO are discussed, and the opto-electrical characteristics of fabricated GaN-based LEDs with graphene/ITO transparent contact are also examined.

2. Experiments

The samples used in this study were all grown on 2-in (0001) patterned sapphire substrates (PSS) via vertical metal organic chemical vapor deposition (CVD). We designed our mask and controlled the etching parameters to achieve a periodic cylindrical pattern with etching depth, cylinder diameter, and spacing of 0.7, 3, and 3 μm, respectively. The whole LED structure was then grown on top of the PSS. Epitaxial layer growth and device process procedures have been described in detail in previous publications [24,25]. High-quality monolayer graphene was synthesized via CVD on copper foil. The CVD-grown graphene was transferred onto the GaN-based LEDs to form the electrical contact. The graphene was first transferred on poly(methyl methacrylate) (PMMA) using the following method. After the deposition of PMMA (4% in anisole) on the graphene by using a spin coater, the PMMA/grapheme/Cu foil was floated on $Fe(NO_3)_3 \cdot 9H_2O$ solution to selective etch the Cu foil. Then, the resultant film with PMMA and graphene was transferred to GaN-based LED substrate, followed by removal of the PMMA using acetone at 60 °C. After transferring graphene on the p-GaN surface, the samples were then prepared for 3.3nm-thick ITO deposition. The self-aligned etching process was performed on the LED wafers to etch out p-GaN and multiple quantum wells partially until the n^+-GaN layer was exposed to generate the mesa. The Cr/Au was deposited onto ITO and n^+-GaN to form the p-type (anode) and the n-type electrodes (cathode), respectively, at the same time. LEDs with ITO transparent contact (LED II) were also prepared to compare with LEDs with graphene/ITO transparent contact (LED I). All fabricated LEDs had a dominant emission wavelength of 453 nm and an area of 270 × 900 μm^2. The current–voltage (*I–V*) characteristics of experimental LEDs were measured using the HP-4156C semiconductor parameter analyzer, and the output powers of the LEDs without epoxy encapsulation were measured with a calibrated integrating sphere at room temperature. The light-emitting intensity images of the LEDs were taken using the calibrated charge-coupled device camera mounted on the microscope.

3. Results and discussion

Figure 1 shows the *I–V* characteristics and dynamic resistances of the LEDs with graphene/ITO transparent contact with annealing temperatures from 300 °C to 600 °C and those of the LEDs with ITO annealed at 500 °C for comparison. Figure 2 shows the 20-mA V_f of the LEDs with graphene/ITO at various annealing temperatures. The conventional LEDs with ITO show a 20-mA V_f of 3.14 V. The LEDs with graphene/ITO transparent contact show a high 20-mA V_f of 4.82 V at an annealing temperature of 300 °C. The 20-mA V_f of LEDs with graphene/ITO transparent contact decreases to 3.05 V when the annealing temperature was increased up to 500 °C. However, the 20-mA V_f increased when the annealing temperature was 600 °C. Besides, the dynamic resistances of the LEDs with graphene/ITO also decreased with increasing the annealing temperature up to 500 °C and went up a little bit

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at 600 °C. LEDs with graphene/ITO annealed at 500 °C shows the lowest 3V-dynamic resistance of 20Ω. The reductions of device dynamic resistance indicate the improved contact resistance of the p-GaN and graphene/ITO interface with annealing. It should be note that the 20-mA V_f of LEDs with the graphene/ITO transparent contact is 0.09 V lower than that of ITO LEDs.

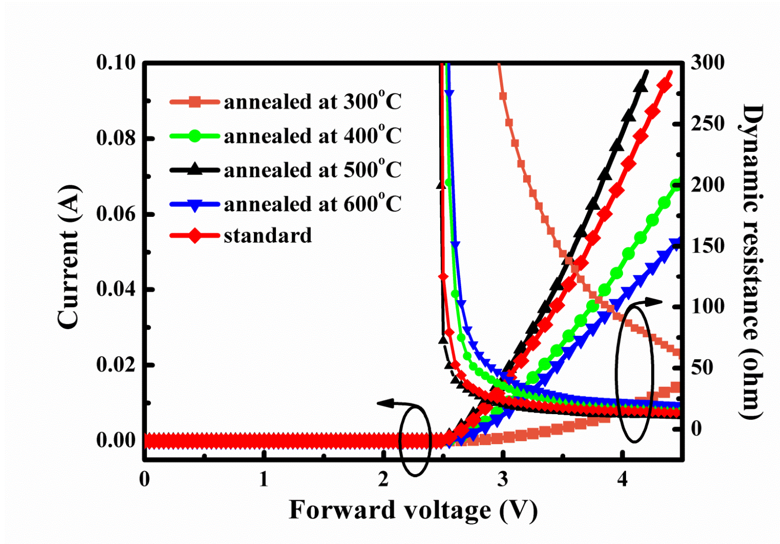

Fig. 1. The *I–V* characteristics and dynamic resistances of the LEDs with graphene/ITO transparent contact with annealing temperatures from 300 °C to 600 °C and the LEDs with ITO annealed at 500 °C.

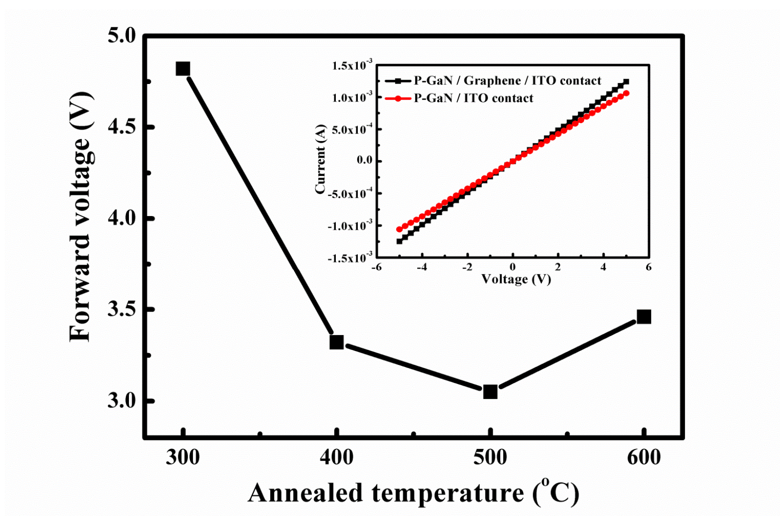

Fig. 2. The 20-mA V_f of the LEDs with graphene/ITO at various annealing temperatures. The inset of Fig. 2 shows the *I–V* characteristics of 500 °C annealed p-GaN/graphene/ITO contact and p-GaN/ITO contact.

We checked the *I–V* characteristics of p-GaN/graphene/ITO contact and p-GaN/ITO contact annealed at 500 °C, as shown in inset of Fig. 2, to determine why the 20-mA V_f of LEDs with graphene/ITO is lower than that of ITO LEDs. The p-GaN/graphene/ITO contact shows an ohmic characteristic after 5 min of annealing at 500 °C in ambient N_2. And the p-GaN/graphene/ITO contact also shows a lower contact resistance than that of the p-

GaN/ITO contact. The specific contact resistance of the p-GaN/graphene/ITO and p-GaN/ITO contacts are 3.72×10^{-3} and 1.52×10^{-2} $\Omega \cdot cm^2$, respectively. The p-GaN/graphene/ITO shows a specific contact resistance that is one order lower than that of p-GaN/ITO. Therefore, LEDs with graphene/ITO (LED I) annealed at 500 °C have lesser 20-mA V_f than that of ITO LEDs (LED II).

Figure 3 shows the measured output power and external quantum efficiency (EQE) as a function of the injection current for LED I and II. All output powers of LEDs increased with increasing injection current. The light output powers and EQE with varying injection currents of LED I was larger than those of LED II. The light output powers of LEDs I and II driven at 20 mA were 21.2 and 19 mW, which correspond to 39.1% and 35.3% EQEs, respectively. Therefore, the 20-mA output power enhancement of LED I is approximately 11% compared with that of LED II. Furthermore, the 200-mA output power of LED I indicates about 19% larger than that of LED II. Efficiency droops (efficiency degradation from the peak of EQE to the EQE of 200 mA) of LED I (28.6%) are less than that of LED II (34.2%). The improvement in the output power and efficiency droop of LED I might be attributed to the decrease in contact resistance of p-GaN/graphene/ITO and the enhancement in current separation by the low lateral resistance of the graphene layer.

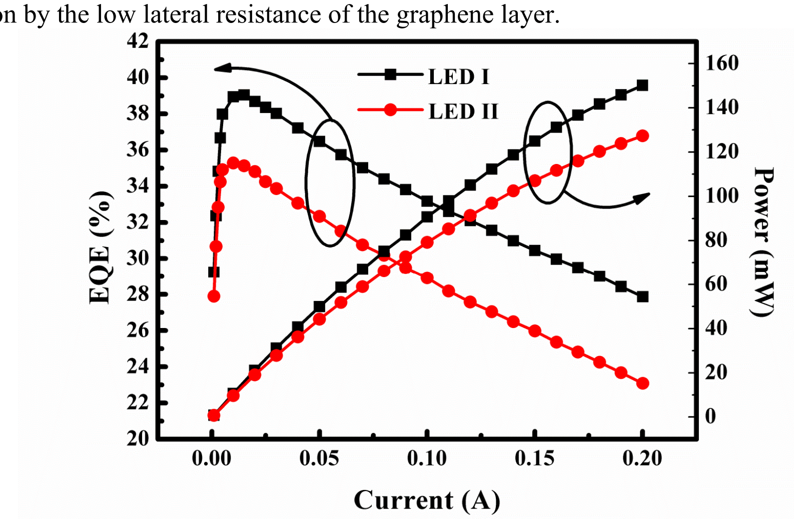

Fig. 3. Output powers and EQE as a function of the injection current for all LEDs.

We studied the near-field emission intensity images of the all LED samples at 20 and 60 mA shown in Fig. 4 to understand the effect of the inserted graphene on current separation. The red color of the images indicates high emission intensity, and the blue color of the images indicates low emission intensity. The 20- and 60-mA near-field images for both samples were taken in the same conditions. The 20- and 60-mA near-field emission intensity images of LED I show a larger high emission intensity area than that of LED II. In addition, the 60-mA near-field images of LED I also show a smaller blue area, which is the low emission intensity region, than that of LED II. The enlarged near-field high emission intensity area of LED I could be attributed to the enhanced current spreading caused by the inserted graphene layer. Theoretically, graphene has a high intrinsic carrier mobility, which is larger than 21,000 $cm^2/V \cdot s$ at room temperature [26,27]. As such, the carrier moves laterally when injected into the graphene layer and the current spreading of LED I is improved. In addition, graphene has a work function of 4.5 eV, which is similar to ITO with a work function of 4.4 eV to 4.5 eV. Hence, their combination gives a low contact resistance to the ohmic junction of LEDs. Figure 5 shows the wall-plug efficiency with the injection currents of LED I and LED II. LED I shows a better wall-plug efficiency than that of LED II because of the lower V_f and larger light output power of LED I than LED II. In addition, the wall-plug efficiency droop of LED I (58%) is less than LED II (66%), which is attributed to the enhanced current spreading and low contact resistance of p-GaN/graphene/ITO.

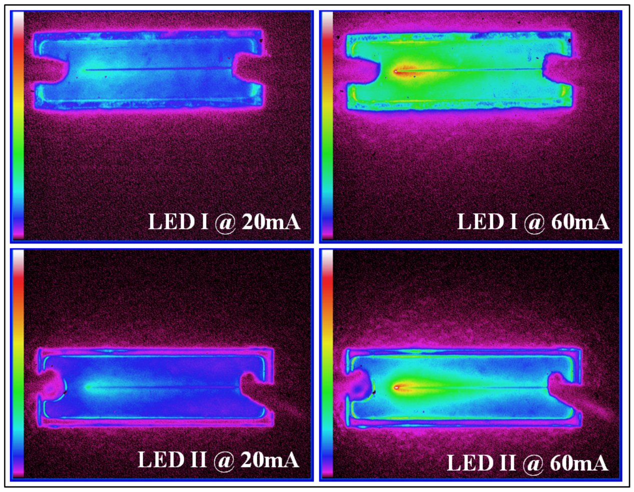

Fig. 4. Near-field emission intensity images of the all LED samples at 20 and 60 mA.

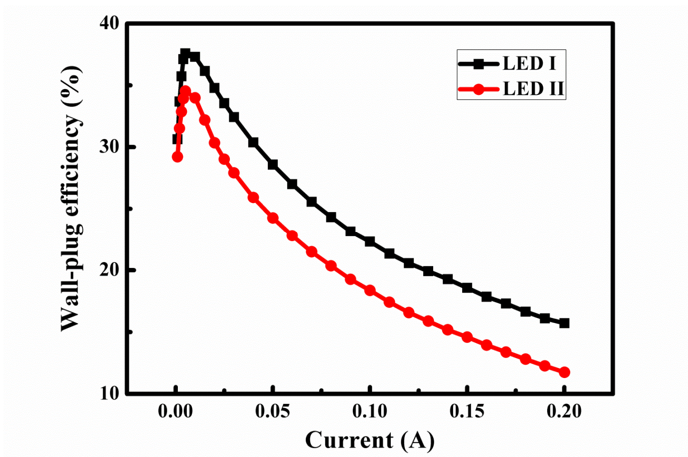

Fig. 5. Wall-plug efficiency with the injection currents of LED I and LED II.

4. Conclusions

In summary, we demonstrated a GaN-based LED with graphene/ITO transparent contact. The ohmic characteristic of the p-GaN and graphene/ITO contact could be preformed by annealing at 500 °C for 5 min. The specific contact resistance of p-GaN/graphene/ITO (3.72×10^{-3} $\Omega \cdot cm^2$) is one order less than that of p-GaN/ITO. In addition, the 20-mA V_f of LEDs with graphene/ITO transparent contact (3.05 V) is 0.09 V lower than that of ITO LEDs (3.14 V). The graphene/ITO transparent contact would also enhance the injection current spreading of the LEDs. Therefore, a 20mA-output power enhancement of 11% can be obtained on LEDs with graphene/ITO transparent contact. The graphene/ITO transparent contact also enhanced the wall-plug efficiency performance of LEDs.

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