

## A self-assembled Ag nanoparticle agglomeration process on graphene for enhanced light output in GaN-based LEDs

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2012 Nanotechnology 23 255201

(<http://iopscience.iop.org/0957-4484/23/25/255201>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 147.47.57.153

The article was downloaded on 04/09/2012 at 08:13

Please note that [terms and conditions apply](#).

# A self-assembled Ag nanoparticle agglomeration process on graphene for enhanced light output in GaN-based LEDs

Jae-Phil Shim<sup>1</sup>, DoHyung Kim<sup>1</sup>, Minhyeok Choe<sup>2</sup>, Takhee Lee<sup>3</sup>,  
Seong-Ju Park<sup>2</sup> and Dong-Seon Lee<sup>1</sup>

<sup>1</sup> School of Information and Communications, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea

<sup>2</sup> School of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Korea

<sup>3</sup> Department of Physics and Astronomy, Seoul National University, Seoul 151-747, Korea

E-mail: [dslee66@gist.ac.kr](mailto:dslee66@gist.ac.kr)

Received 19 March 2012, in final form 30 April 2012

Published 31 May 2012

Online at [stacks.iop.org/Nano/23/255201](http://stacks.iop.org/Nano/23/255201)

## Abstract

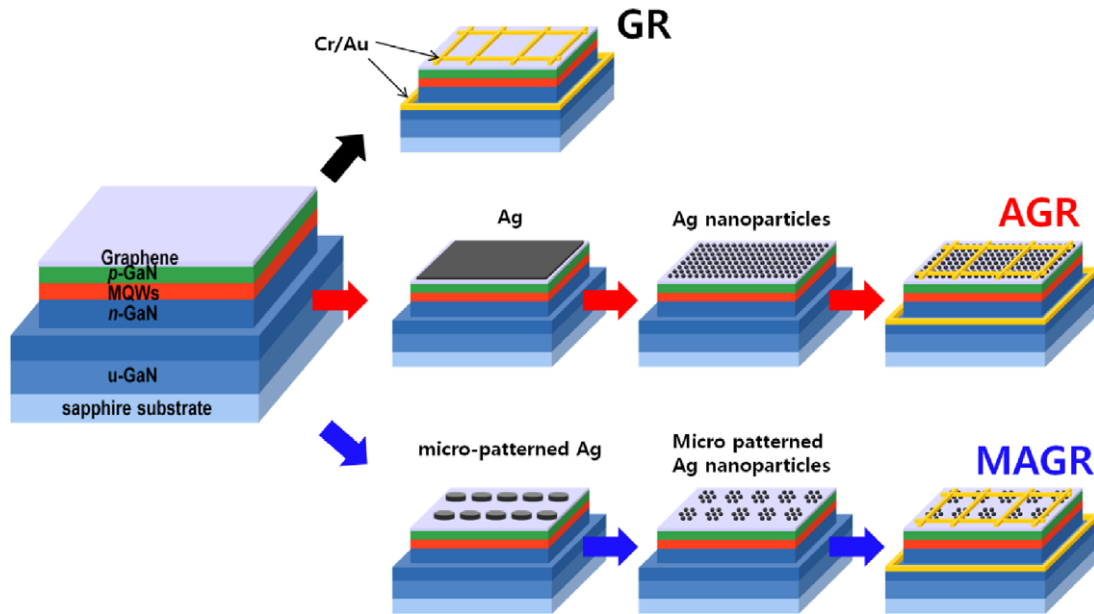
We introduce Ag nanoparticles fabricated by a self-assembled agglomeration process in order to enhance the electrical properties, adhesive strength, and reliability of the graphene spreading layer in inorganic-based optoelectronic devices. Here, we fabricated InGaN/GaN multi-quantum-well (MQW) blue LEDs having various current spreading layers: graphene only, graphene with Ag nanoparticles covering the surface, and graphene with Ag nanoparticles only in selectively patterned micro-circles. Although the Ag nanoparticles were found to act as an additional current path that increases the current spreading, optical properties such as transmittance also need to be considered when the Ag nanoparticles are combined with graphene. As a result, LEDs having a graphene spreading layer with Ag nanoparticles formed in selectively patterned micro-circles displayed more uniform and stable light emission and 1.7 times higher light output power than graphene only LEDs.

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Graphene, composed of a two-dimensional (2D) honeycomb lattice of carbon atoms, has attracted great interest due to its excellent optical, electrical, and material properties, which include high transparency, electrical conductivity, thermal conductivity, mechanical and chemical stability, and flexibility [1, 2]. In particular, the high transparency from ultraviolet (UV) to infrared (IR) wavelengths and outstanding electrical properties of graphene have fascinated researchers in their attempts to apply graphene as a transparent electrode for solar cells or light emitting diodes (LEDs) [3, 4]. Graphene usually has excellent coherence with organic-based materials, making it convenient to use organic-based devices

by simply coating them with an aqueous graphene solution or by the physical transfer of graphene grown by chemical vapor deposition (CVD). For this reason, many applications of graphene transparent electrodes have been reported for organic solar cells and organic LEDs [5–7]. To date, there have been comparatively few reports pertaining to GaN-based optoelectronic device applications due to the low adhesive strength and contact problems between graphene and inorganic materials. Of these, Jo *et al* [8] first applied graphene as a transparent current spreading layer in GaN-based blue LEDs and demonstrated the possibility of using it as an alternative transparent material to indium tin oxide (ITO). Application of graphene in LEDs could overcome the limitations of using an ITO transparent layer such as



**Figure 1.** Fabrication process of blue LEDs with various current spreading layers, including graphene only (GR), graphene with Ag nanoparticles on the whole surface (AGR), and graphene with Ag nanoparticles only in selectively patterned micro-circles (MAGR).

increased cost due to indium scarcity, and difficulties in flexible applications due to cracking and breaking problems. Furthermore, the workfunction of graphene is easily tuned from 4.3 to 5 eV by introducing metallic doping so that graphene can reduce the contact resistance with p-GaN more than ITO by lowering the Schottky barrier height (SBH). However, GaN-based LEDs with graphene actually display inefficient current injection due to their higher contact and sheet resistance than ITO such that the light emission is not uniform, but rather is strong only near the p-metal region. Furthermore, the performances of LEDs having graphene spreading layers rapidly deteriorate under high current injection due to the degradation of graphene [8, 9]. All things considered, there are still limitations in using graphene in GaN-based LEDs, such as having a lower performance, in addition to worse reliability and stability, than when using an ITO current spreading layer. To overcome these problems, in this study we introduced silver (Ag) nanoparticles onto the graphene via a self-agglomeration process, and then applied the Ag-nanoparticle-combined graphene as a current spreading layer onto InGaN/GaN blue LEDs. Moreover, to further increase the light extraction efficiency we intentionally formed the Ag nanoparticles in selected micro-sized circles on the graphene.

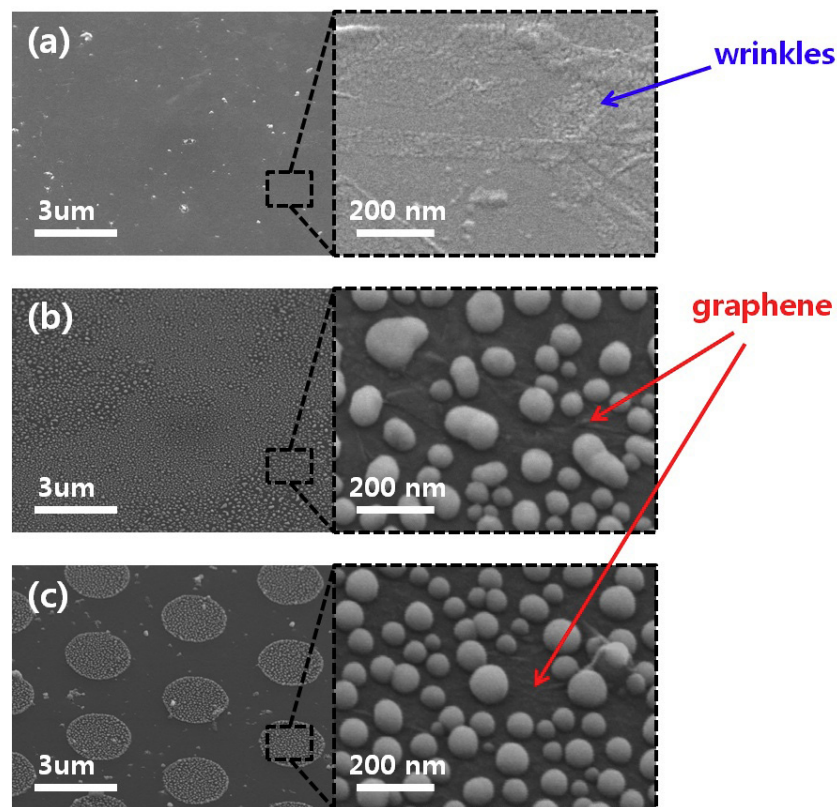
## 2. Fabrication

InGaN/GaN multi-quantum-well (MQW) LED structures were grown by metal organic chemical vapor deposition (MOCVD). The epitaxial structure consisted of an undoped GaN/Al<sub>2</sub>O<sub>3</sub> template, a 2 μm Si-doped n-type GaN layer, a seven-period In<sub>0.15</sub>Ga<sub>0.85</sub>N/GaN (3 nm/8 nm) MQW layer, and a 100 nm Mg-doped p-type GaN layer. Using CVD, multi-layer graphene was grown separately on a 300 nm

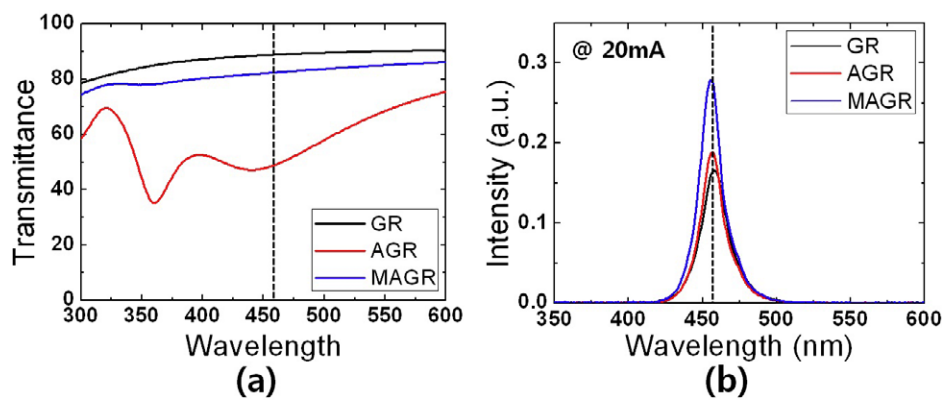
thick nickel (Ni) substrate at 1000 °C under CH<sub>4</sub> gas flow, with 4% H<sub>2</sub> applied as the Ar gas mixture for 5 min. The Ni substrate was etched in an aqueous iron chloride (FeCl<sub>3</sub>) solution; subsequently, graphene released from the Ni substrate was transferred onto the top surface of the epitaxial structure as a current spreading layer. Note that we have demonstrated the characteristics of graphene in our previous works [10, 11]. Covered with a photoresist (PR) mask, the graphene and GaN layers were etched using reactive ion etching (RIE) and inductive coupled plasma etching (ICP) until n-GaN was revealed. On this structure, we then fabricated three types of blue LED, each having different current spreading layers: graphene only (GR), Ag nanoparticles covering the entire graphene surface (AGR), and selectively patterned micro-circle Ag nanoparticles on the graphene surface (MAGR) (figure 1). For the LED with the AGR sample, we deposited 10 nm of Ag onto the graphene using an electron beam evaporator. For the MAGR sample, 10 nm of Ag was deposited onto the graphene in a micro-circle pattern that had a 2 μm diameter and 4 μm period. Then, both the AGR and MAGR samples were annealed in a rapid thermal annealing (RTA) machine under N<sub>2</sub> ambient at 600 °C for 5 min in order to form Ag nanoparticles. As a final step, Cr/Au (30 nm/ 300 nm) was deposited as the p- and n-contact pads for all samples.

## 3. Results and discussion

Figure 2 presents scanning electron microscope (SEM) images of all the current spreading layers used in this study. Multi-layer graphene was well transferred onto the p-GaN and wrinkle boundaries were observed, as shown in figure 2(a). It can also be seen that while Ag nanoparticles are observed on the entire surface area of the graphene for the



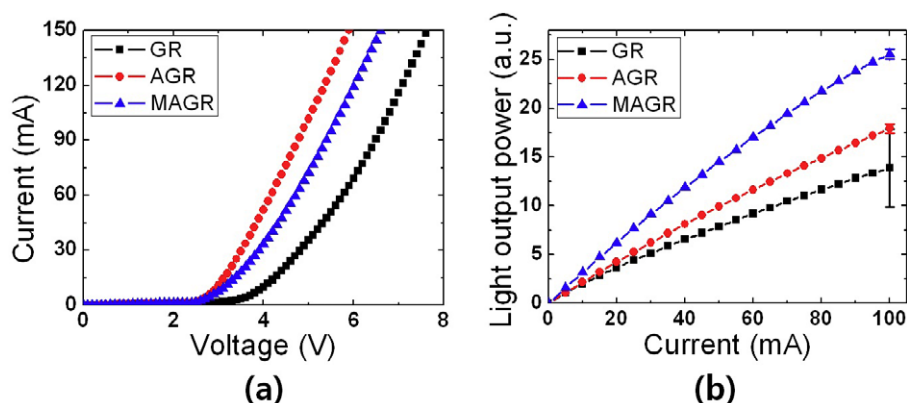
**Figure 2.** SEM images of (a) graphene only (GR), (b) graphene with Ag nanoparticles on the whole surface (AGR), and (c) graphene with Ag nanoparticles only in selectively patterned micro-circles (MAGR).



**Figure 3.** (a) The transmittances of the GR, AGR and MAGR current spreading layers on a double polished sapphire substrate. (b) The electroluminescence values for the fabricated LEDs at 20 mA current injection.

AGR sample, they are only observed in the selective circle areas on the graphene in the MAGR sample (figures 2(b) and (c)). In both cases, the graphene layers showed no damage under the Ag nanoparticles, as the arrow indicates. The Ag nanoparticles were formed by a self-organized agglomeration process during which the 10 nm thin Ag layer deposited on the graphene was changed to nanoparticles through an RTA process [12, 13]; heat transfer from a heated substrate to a metallic film is critical for this agglomeration process. Since graphene has a high thermal conductivity, it delivers heat well from the GaN to the thin Ag layer, enabling the Ag nanoparticles to be formed on the graphene layer nearly

without loss [14]. It is interesting to note that the shapes of the Ag nanoparticles were irregular and that their sizes in the AGR sample were diverse, ranging from 50 to 200 nm (figure 2(b)). On the other hand, the MAGR sample displayed relatively regular hemispherical Ag nanoparticle shapes in the micro-circle patterned area, with sizes ranging from 50 to 100 nm (figure 2(c)). Generally, the agglomeration process is driven by lowering the total energy of the system with respect to the lowest energy of the interface between the metal nanoparticles and the substrate [15, 16]. Furthermore, the surface topography of the substrate, such as the patterning and crystallographic orientation, has a large influence on the



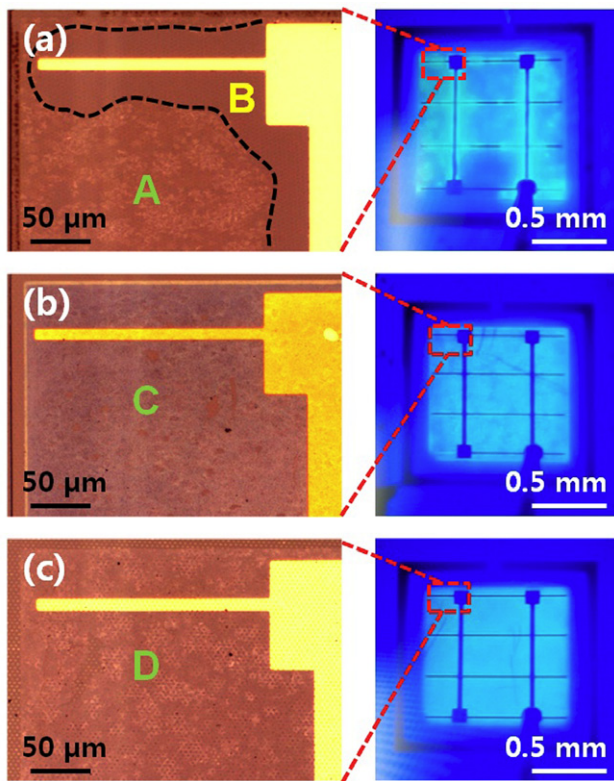
**Figure 4.** (a) The current–voltage characteristics of the fabricated LEDs. (b) The light output power values for the LEDs for different current spreading layers. The error bar for the ‘GR’ indicates a big chip-to-chip EL intensity variation due to poor adhesion of the graphene.

formation of metal nanoparticles; thus, the MAGR sample shown here could form a more ordered shape and regular size of Ag nanoparticles than the AGR sample (since the agglomeration started from regular circular patterns) [16].

To investigate the optical properties of each current spreading layer, we measured the transmittance by using a double polished sapphire substrate as the reference. In figure 3(a), GR and MAGR showed over 80% and over 75% transmittance for the measured wavelength range, respectively. MAGR showed a similar shape to GR, though with lower transmittance, which is believed to be due to the shaded area of the micro-patterned Ag nanoparticles. AGR, however, showed a severe transmittance fluctuation. Generally, metal nanoparticles are known to absorb specific wavelengths of light depending on their size and period; as the size of the nanoparticles increases, specific wavelength absorptions shift to the red [17, 18]. For the AGR sample, the dominant nanoparticle sizes of 50 and 200 nm over the entire graphene area resulted in transmission dips at the 360 and 450 nm wavelengths. Although MAGR also contained Ag nanoparticles, the particles did not sufficiently cover the surface to show the transmission fluctuation, though we can still see a small dip near 360 nm. At 460 nm, corresponding to the emission wavelength of the fabricated LEDs, the transmittances of the GR, AGR and MAGR layers were measured to be 89%, 49% and 82%, respectively. Figure 3(b) shows the electroluminescent (EL) intensities of the fabricated devices. All samples exhibited similar EL spectra shapes, with a  $\sim$ 460 nm dominant peak wavelength at a 20 mA current injection, though with different EL intensities. The interesting point is that although the GR sample displayed the highest transmittance of 89% at 460 nm, the MAGR sample, having a transmittance of 82%, showed the strongest EL intensity. Moreover, although the AGR sample had only 49% transmission at 460 nm, it had an even higher EL intensity than the GR sample. Thus, we posit here that the EL performance depends not only on optical properties such as transmittance, but also on electrical properties that include current spreading. To further investigate the EL performance, we subsequently analyzed the current–voltage ( $I$ – $V$ ) characteristics.

Figure 4(a) presents the  $I$ – $V$  characteristics of the fabricated devices. The turn on voltages at 20 mA current injection were 3.2 V, 3.4 V and 4.5 V for LEDs with AGR, MAGR and GR current spreading layers, respectively. The 4.5 V turn on voltage at 20 mA for the GR sample is almost the same as the reported results for LEDs fabricated using a graphene spreading layer [8, 9]. As the number of Ag nanoparticles increased (AGR > MAGR > GR) on the graphene, the electrical properties in the LEDs such as the series resistance were enhanced. The calculated series resistances of LEDs with AGR, MAGR and GR at a 20 mA current injection were 10  $\Omega$ , 25  $\Omega$  and 70  $\Omega$ , respectively. In this case, the Ag nanoparticles likely act as a conductor and electrical bridge between the graphene interlayers, even at the wrinkle boundary, such that the Ag nanoparticles reduced the series resistance of the LEDs by increasing the conductivity and additional current spreading paths of graphene [19, 20]. Figure 4(b) shows the light output power values for LEDs having current spreading layers as a function of current injection, where it is seen that the light output power of all samples increases monotonically similarly to that in conventional LEDs. Also, the EL enhancement of AGR and MAGR is demonstrated through a better current spreading than for GR, exceeding their transmission losses at the emission wavelength of 460 nm. Among the three samples, the LEDs with MAGR had the highest output power, which was 1.7 times stronger than the LEDs with GR at a 100 mA current injection. This result is due to the optimized optical and electrical properties of MAGR, such as a relatively higher transmittance of 82% at a 460 nm wavelength compared to AGR and improved current spreading compared to GR. It is also interesting to note that the LEDs with GR spreading layers showed large chip-to-chip variation in EL emissions, whereas the LEDs with AGR and MAGR showed a stable and steady emission, thereby indicating that the adhesion of graphene was improved by introducing Ag nanoparticles, as can be seen better in figure 5.

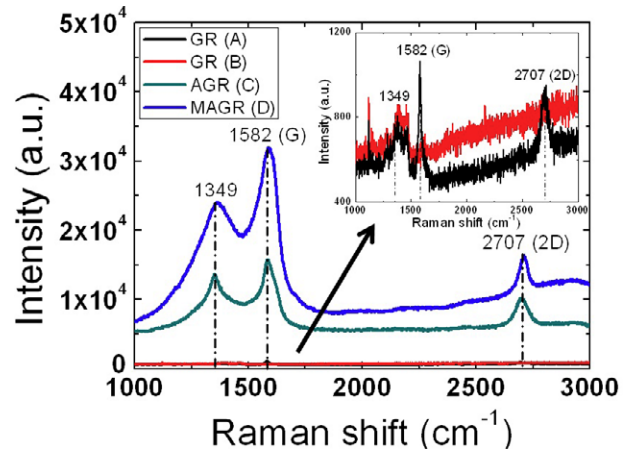
In figure 5, there is a bright and uniform light emission in LEDs with AGR and MAGR in the top layer at a 5 mA current injection. However, the light emission is not uniform on the GR sample but stronger near the p-type metal electrode



**Figure 5.** Optical images of light emission at 5 mA for fabricated LEDs with (a) GR, (b) AGR and (c) MAGR current spreading layers. The right columns show magnified images. In (a), 'A', 'C' and 'D' are regions where graphene remains and 'B' indicates where graphene has been torn off. Of special note, 'D' is the micro-circle patterned region. While the emission of the GR sample is not uniform, the AGR sample emits light more uniformly and MAGR is the most uniform.

due to incomplete current spreading. In the magnified optical images on the left side of the figure, whereas there is only a small amount of graphene remaining in the GR sample, the LEDs with AGR and the MAGR are seen to have graphene completely covering the top surface.

In figure 6, the Raman spectrum is used to investigate positions 'A', 'B', 'C' and 'D' of figure 5 to further clarify the characteristics of graphene to determine whether graphene remains or not. Two main peaks of graphene corresponding to the G peak ( $\sim 1582\text{ cm}^{-1}$ ) and the 2D peak ( $\sim 2707\text{ cm}^{-1}$ ) were observed at the points 'A', 'C' and 'D'. However, the G and 2D peaks were not found at point 'B' near the p-type metal electrode in the GR sample. We tentatively posit that whereas the Ag nanoparticles on the graphene of the AGR and MAGR samples are annealed in the RTA machine, the thin Ag layer changes to nanoparticles and pins the graphene by diffusing into the p-GaN, thereby improving the adhesive strength between the p-GaN and the graphene. Note that further study is currently being conducted in order to investigate and characterize this improvement in adhesion. In the GR sample, however, graphene near the p-type metal region is easily torn off during the fabrication process due to the weak adhesion. This partially torn graphene induces inefficient current spreading



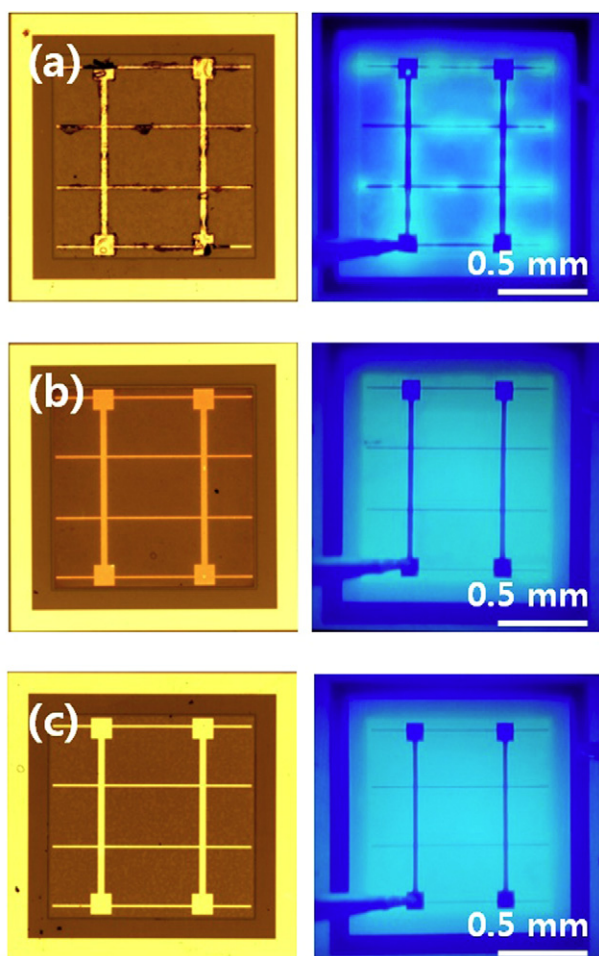
**Figure 6.** Comparison of the Raman spectrum of points 'A', 'B', 'C' and 'D' from figure 5.

and a large chip-to-chip fluctuation in the light output power. We also observed an over 10 times stronger Raman intensity enhancement at 'C' and 'D' than at 'A' in the remaining graphene regions. The Ag nanoparticles on the graphene of the AGR and MAGR samples coupled with the laser wavelength of 514 nm such that the surface plasmon resonance (SPR) of the Ag nanoparticles played a dominant role in enhancing the Raman intensity, which is referred to as surface enhanced Raman scattering (SERS) [21, 22]. Furthermore, the Ag nanoparticles, which were more regular and spherical in the micro-circle patterned area of the MAGR sample, resulted in the largest Raman enhancement. This phenomenon confirmed that the self-organized agglomeration of Ag nanoparticles on graphene could also be utilized in SPR-combined optoelectronic devices.

Figure 7 presents optical images of the un-biased condition (left column) and light emission at 20 mA of current injection (right column) for each current spreading layer after 350 mA of high current operation. The p-type contact pad of GR had severe damage (shown as the dark spots in the left figure) because the high power (350 mA current injection) became focused only on the metal due to the current being inefficiently spread by the partially remaining graphene. As a result, GR displayed even weaker light emission near the p-type metal at 20 mA current injection than at 5 mA, prior to the high current injection. However, AGR and MAGR both displayed uniform and steady light emission even after high power operation. These results indicate that reliable and stable light emission could be confirmed in GaN-based LEDs by using Ag nanoparticles that were combined with a graphene current spreading layer.

#### 4. Conclusions

In conclusion, we fabricated blue LEDs with different current spreading layers (GR, AGR and MAGR). Ag nanoparticles were then formed by a self-agglomeration process on the graphene, and were found to enhance the electrical properties of the graphene in terms of reducing the series resistance and improving the current spreading by acting as an additional



**Figure 7.** Optical images of LEDs with (a) GR, (b) AGR and (c) MAGR current spreading layers after 350 mA high current injection (left column) and their light emission at 20 mA current injection (right column).

current path and strengthening the adhesion between the graphene and the p-GaN. Furthermore, the Ag nanoparticles on the graphene were confirmed to provide reliable and stable light emission in GaN-based LEDs, although the transmission losses still need to be improved for efficient light extraction. Nevertheless, the LEDs with a graphene spreading layer showed 1.7 times higher light output power when combined with micro-patterned Ag nanoparticles. It is expected that the formation of Ag nanoparticles on graphene could be utilized in a diverse range of optoelectronic devices, including LEDs and solar cells. Moreover, choosing a proper type of metal and optimizing the size and period (e.g. smaller nanoparticle

size and more periodic) of the metal nanoparticles may further increase device performance, potentially enabling their application in SPR-combined devices.

## Acknowledgments

This work was supported by the Energy Resource R&D program (No. 20102010100020) under the Ministry of Knowledge Economy and by the Ministry of Education, the National Research Foundation (NRF) grant funded by the Korean government (MEST) (No. 20110004694). This work was supported by the Ministry of Land, Transport, and Maritime Affairs (Grant No. 20090006).

## References

- [1] Geim A K and Novoselov K S 2007 *Nature Mater.* **6** 183
- [2] Castro Neto A H, Guinea F, Peres M R, Novoselov K S and Geim A K 2009 *Rev. Mod. Phys.* **81** 109
- [3] Bonaccorso F, Sun Z, Hasan T and Ferrari A C 2010 *Nature Photon.* **4** 611
- [4] Pang S, Hernandez Y, Feng X and Mullen K 2011 *Adv. Mater.* **23** 2779
- [5] Wang X, Zhi L and Mullen K 2008 *Nano Lett.* **8** 323
- [6] Wu J, Agrawal M, Becerril H A, Bao Z, Liu Z, Chen Y and Peumans P 2010 *ACS Nano* **4** 43
- [7] Reina A, Jia X, Ho J, Nezich D, Son H, Bulovic V, Dresselhaus M S and Kong J 2009 *Nano Lett.* **9** 30
- [8] Jo G *et al* 2010 *Nanotechnology* **21** 175201
- [9] Kim B J, Lee C, Jung Y, Baik K H, Mastro M A, Hite J K, Eddy C R Jr and Kim J 2011 *Appl. Phys. Lett.* **99** 143101
- [10] Choe M *et al* 2010 *Org. Electron.* **11** 1864
- [11] Shim J P, Choe M, Jeon S R, Seo D, Lee T and Lee D S 2011 *Appl. Phys. Express* **4** 052302
- [12] Yeh D M, Huang C F, Chen C Y, Lu Y C and Yang C C 2008 *Nanotechnology* **19** 345201
- [13] Song Y M, Choi E S, Park G C, Park C Y, Jang S J and Lee Y T 2010 *Appl. Phys. Lett.* **97** 093110
- [14] Balandin A A, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F and Lau C N 2008 *Nano Lett.* **8** 902
- [15] Kojima Y and Kato T 2008 *Nanotechnology* **19** 255605
- [16] Kim D, Giermann A L and Thompson C V 2009 *Appl. Phys. Lett.* **95** 251903
- [17] Lee K C, Lin S J, Lin C H, Tsai C S and Lu Y J 2008 *Surf. Coat. Technol.* **202** 5339
- [18] Mock J J, Barbic M, Smith D R, Schultz D A and Schultz S 2002 *J. Chem. Phys.* **116** 6755
- [19] Tien H W, Huang Y L, Yang S Y, Wang J Y and Ma C C M 2011 *Carbon* **49** 1550
- [20] Seo T H *et al* 2011 *Appl. Phys. Lett.* **98** 251114
- [21] Zhou H, Qiu C, Yu F, Yang H, Chen M, Hu L and Sun L 2011 *J. Phys. Chem. C* **115** 11348
- [22] Lee J, Novoselov K S and Shin H S 2010 *ACS Nano* **5** 608